A STUDY OF THE ENCAPSULATION
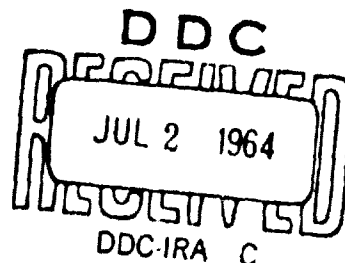# OF HIGH ENERGY SUBSTANCES

CONSTANTINE C. PETROPOULOS

CAPSULAR RESEARCH AND PRODUCT DEVELOPMENT DEPARTMENT

THE NATIONAL CASH REGISTER COMPANY

APRIL 1964

OFFICE OF NAVAL RESEARCH

Final Report (April 1, 1959 to December 31, 1963)

A STUDY OF THE ENCAPSULATION OF
HIGH ENERGY SUBSTANCES

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Capsular Research and Product Development
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The National Cash Register Company

Contract No. NOnr 2848 (00)

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Final Report (April 1, 1959 to December 31, 1963)
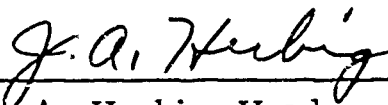

Prepared By: _____

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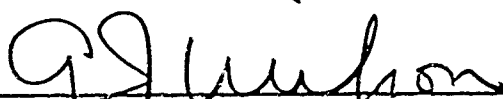

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TABLE OF CONTENTS

INTRODUCTION

A number of years ago, The National Cash Register Company successfully applied the phenomenon of coacervation to micro-encapsulation of a variety of substances. Since this encapsulation was carried out in an aqueous solution, it was limited to those substances which are largely insoluble in, or unreactive with, water. For the past several years, research has been conducted to remove these restrictions from the NCR encapsulation method.

In 1959, a research program sponsored by the U. S. Navel Bureau of Weapons (BuWep) was being conducted which had, as its objective, the encapsulation of high energy solid materials which are useful as components of a solid propellant formulation. A large number of these potentially useful substances had to be protected from the reaction with water vapor or water during processing and in the cured grain. It was felt that by encapsulating the water sensitive solids this problem could be overcome.

The difficulties encountered in achieving a polymeric capsule wall having a high level of impermeability to water or other small polar molecules pointed out a need for a thorough understanding of the basic phenomenon involved in encapsulation and of the mechanism of permeability. For this reason, the Office of Naval Research (ONR) supported the effort which is described herein. In addition, the Office of Navel Research was interested in the encapsulation of highly energetic liquid propellants in contrast to the encapsulation of solids.

The ultimate aim of the ONR program was to extend basic microencapsulation knowledge to the encapsulation of highly energetic liquid propellants. Here again, the severe restriction for use of these liquids was

their sensitivity to water or water vapor. Hopefully, encapsulation could not only convert these liquids to pseudosolids but also afford to the liquids adequate protection to water or water vapor.

In order to encapsulate these liquids a suitable polymeric wall material had to be chosen. This wall material had to have the following properties:

1. Polymer does not react with liquid fuel to be encapsulated.

2. The Polymer could be used in the encapsulation process or a new encapsulation process had to be developed.

3. The Polymer should be impermeable to the liquid fuel as well as water or water vapor.

4. The Polymer must have the appropriate strength characteristics and be compatible with the other components of a propellant formulation.

The above points stressed the need for a vast amount of basic research in the area of fuel encapsulation.

Early efforts of the program have clarified some areas requiring definitions of basic mechanisms. Initial work was directed towards the understanding of basic factors responsible for small molecules permeating polymeric films. Progress has been made in this area. In addition, research was conducted in the area of encapsulation. This research included the study of basic mechanisms associated with encapsulation, compatibility of polymers with potential liquid fuels (eg hydrazine), synthesis of new polymers, and the encapsulation of liquid fuels or model compounds.

This report is a summary of the work conducted under Contract No. NOnr 2848 (00) entitled "A study of the Encapsulation of High Energy Substances". The report is divided into two parts. Part I will be of a general

-2-

nature summarizing the total program from April 1, 1959 to December 31, 1963. Part II will cover the specific effort from June 30, 1962 to December 31, 1963. For specific details of the experimental effort from April 1, 1959 to June 30, 1962, the Interim Reports should be consulted.

PART I   SUMMARY OF RESEARCH PROGRAM

    A.   Film Permeability Studies

        1.   Parameters [1]

The permeability of ethylcellulose and nitrocellulose to thirteen different gases and vapors was determined. The solubility of these gases and vapors in ethylcellulose and nitrocellulose was also measured by gravimetric and volumetric methods of equilibrium sorption. The diffusion constants of the gases and vapors were calculated from the permeability and solubility data obtained by the relation, $P = DS$ where P and S are the permeability and solubility respectively and D is the diffusion constant. The log D was found to decrease linearly with an increase of log M where M is the molecular weight of the penetrants. The shape of the molecules also played an important role in the diffusion process. It was also found that the log S increased linearly with an increase in the Lennard-Jones force constants. (See Interview Report No. 2, 1 April, 1960 to 31 December, 1960). It is possible, therefore, once these relationships are established from a few experimental points, to predict the permeability of a number of penetrants through a given film from the physical properties of the penetrant.

-3-

Polar groups in a polymer material tend to increase the water permeation of the material. The effect of organo-metallic crosslinking agents on polymethacrylic, ethylcellulose and nitrocellulose films on water permeability were inconclusive.

2. Water Permeability of Polymer Films

The water permeability of several commercial polymer films and some synthetic polyamide films have been determined and in most cases was found to be too high for any practical use. However, the permeability of water through commercial Saran and Kel-F films was greatly reduced indicating that films with a hydrocarbon type backbone warranted further investigation. The permeability of the synthetic polyamide films towards water was of the same order of magnitude as that of ethylcellulose, a highly permeable film. The commercial nylon (6.6) and nylon (6, 10) showed a reduction of water permeation of about one third that of ethylcellulose. These two films were prepared by compression molding of the commercial molding powder and were somewhat thicker in diameter than the other films which were compared.

B. Compatibility of Polymers With Hydrazine

One of the necessary and essential conditions for the encapsulation of hydrazine would be compatibility with candidate wall materials. The compatibility of hydrazine with 24 polymers was tested. This was accomplished by determining the melting point of the polymers before and after immersion in hydrazine for 78 days and by weighing the polymer before and after immersion in hydrazine. The amount of hydrazine absorbed by the polymer would give information necessary to

-4-

estimate the permeability of hydrazine, since solubility is closely related to permeability. A polymer was considered compatible with hydrazine, if after the immersion period there was no change in melting point and no gain or loss in weight. Polyethylene, ethylcellulose, acrylic and nylon resins were among those polymers which were compatible with hydrazine. Polymers containing halogen such as Saran and Kel-F, although good water barriers, were attacked by hydrazine. Contact of nitrocellulose with hydrazine resulted in self-ignition and explosive combustion. Many polymers such as polyvinyl acetate were swelled and degraded while others such as polyacrylamides and polyacrylamine formed gels.

It was a difficult task to find a polymer that would not be attached, swelled or degraded by hydrazine and at the same time offer low permeability characteristics.

C.   Synthetic Polymer Studies

1. Polyamides

It was difficult to measure water permeability of polyamide films formed in situ at an interface during an interfacial polymerization because these films were highly swollen and not mechanically rigid enough to remove from the interface as a film for permeability measurements. The polymers were therefore prepared by interfacial polymerization, coagulated, purified and isolated. These purified polymers were then redissolved and cast as films for permeability measurements. These films were no longer in the swollen state and the water permeability would not be the same as that of the swollen films formed in situ, but the data did serve as a guide in screening possible

candidate polyamide films. The water permeability of these films has already been discussed above.

2. Two Stage Polymer Studies

In order to simultaneously study the effect of films approaching a hydrocarbon type structure and of crosslinking on water permeation, polyvinyl cinnamate was prepared and cast from solution as a film. The water permeability of this film was measured. This same film was then photocrosslinked and the water permeability compared with that of the uncrosslinked film. It was found that the water permeability of the crosslinked film was about one half that of the uncrosslinked film.

At this time, it was thought that a promising approach to encapsulation would be through a two stage polymerization process. This could involve the deposition of a soluble linear prepolymeric wall containing reactive sites around an internal phase by some type of phase separation, followed by crosslinking the wall.

In order to get some idea of the speed of a free radical type crosslinking reaction, the rate of photopolymerization of a difunctional monomer in the bulk using desylaryl sulfides as photoinitiator was studied.[2] The difunctional monomer studied was tetraethylene glycol dimethacrylate. The monomer was used in the bulk to take advantage of the autoacceleration of a polymerization due to the increase of viscosity in the medium as polymerization occurs. This is better known as the "Trommsdorff" or "gel" effect. Since gelation occurs earlier when crosslinking occurs, the inception of the autoaccelerated rate occurs

almost instantenously in the polymerization of a difunctional monomer in the bulk. This was found to be the case for the monomer studied and complete gelation and crosslinking occured in about one minute. It was also found that the rate of polymerization initiated by desyl-aryl sulfides with electron releasing substituents was about five times faster than desylphenyl sulfide, the unsubstituted compound.

The rates of polymerization of a difunctional monomer in the bulk was studied also, because it was assumed that the same conditions responsible for the autocatalytic effect of a difunctional mono-mer in the bulk would also exist in a polymer film about to be cross-linked and the rates should be comparable. The time, therefore, of post treating a capsule wall by free radical crosslinking should be about the same as a bulk polymerization of a difunctional monomer.

The next problem was to prepare prepolymers which were solu-ble and still contained an active group. This was done by choosing a polymerization mechanism in which one group would be preferentially polymerized and the other would remain unreacted and capable of being crosslined at some later time. For example, a vinyloxy double bond can be polymerized rapidly under cationic condition by Lewis acids and under these conditions a methacrylic double bond would be unreactive. The methacrylic double bond can then be crosslinked by a free radical initiated by polymerization mechanism. The sequence could also be reversed. The monomers with this duality in polymeri-zation mechanism were either synthesized or obtained commercially and the mode of polymerization studied. Two stage soluble polymers were prepared that could be independently crosslinked at a later time. Some capsular walls were formed by these polymers, but were not

-7-

mechanically rigid enough to isolate and post treat, or on post treatment formed aggregated gels.

D. Encapsulation Studies

1. Interfacial Energy

Certain encapsulation techniques require that the material to be encapsulated be dispersed in a polymeric solution in particulate form. This is followed by a step which causes the polymer to phase out of solution as a liquid resulting in a three phase system of solvent, material to be encapsulated (Internal Phase), and a concentrated polymeric solution. This concentrated polymeric solution then deposits at the solvent - Internal Phase - interface resulting in a capsule.

It was felt that interfacial energy was an important quantity in establishing the essential conditions for the accumulation of a micromolecule around a dispersed liquid droplet in the encapsulation process. In order for encapsulation to be successful, the encapsulating material must selectively deposit itself around the internal phase as a fluid mass, which is subsequently hardened by various techniques into a rigid film. This implies that the encapsulating material must have a greater affinity for the internal phase to be encapsulated than for other surfaces in its environment, i.e., the interfacial tension (interfacial energy) between internal phase and encapsulating phase must be smaller than the interfacial tension between the internal phase and dispersing medium. A relationship showing this was derived and interfacial tensions were measured between the three phases - wall phase, internal phase, vehicle phase - for systems where encapsulation proceeded quite nicely and for those systems in which encapsulation did not occur.

Interfacial tensions were measured not only to determine the value of the difference discussed above ($\gamma_{1-2} - \gamma_{1-3}$) (1, internal phase; 2, encapsulating phase; 3, vehicle phase), but also were used to calculate the "work of adhesion" and the "spreading coefficient" which are also important quantities in encapsulation phenomena. The interfacial energy difference appears to be an important factor. The general statement that the encapsulation will be easier when the difference is more positive, however, may be classed in a category that a mathematician would call a "necessary but not sufficient" condition. The data may, however, be used as a guide in choosing the right system for encapsulation of a given liquid. It also points out that when a difficulty in encapsulation is encountered, the difficulties may possibly be alleviated by controlling the boundary tension by the application of surfactants.

2. Dispersion Stability

Certain techniques of encapsulation employ a liquid supporting vehicle in which the internal phase must be maintained in a dispersed droplet form during the encapsulation period. Since the materials of interest are either reactive with, or soluble in water, chemical compatible non-aqueous dispersing vehicles were sought. Many attempts to encapsulate water miscible liquids have been unsuccessful chiefly because of the difficulty in obtaining a stable dispersion.

It has been reported that for oil in water emulsions, instability results when the appropriate spreading coefficient is positive, optimum stability is obtained when the coefficient is barely negative. For water in oil emulsions, the indications are that the most negative value obtainable is the optimum one. It was desirable to see whether these

findings applied to non-aqueous systems which is of more interest here.

There appeared to be no relationships between spreading coefficient and dispersion stability on systems measured. It was found, however, that some of the span series of surfactants gave stable dispersions of hydrazine in fluoro-carbon -43.

3. Phase Separation

The use of two stage polymers in conjunction with phase separation techniques was discussed briefly above and is covered in more detail in the latter part of the report. In all cases either a flexible, mechanically unstable wall was formed or on post treatment of the wall, in situ aggregation and gelling of the particles resulted. Miscellaneous phase separation techniques that were tried were unsuccessful.

4. Interfacial Polymerization

Attempts to encapsulate an aqueous solution of a diamine by reacting at an interface with an acid chloride resulted in thin polymeric skins not mechanically rigid enough for handling. In some cases, it was possible to protect the aqueous diamine internal phase for about two weeks with a second coat of parafin wax. Similar results were obtained when a diamine was used in the absence of water serving both as an internal phase and an acid acceptor in the interfacial polymerization process. When hydrazine was injected into a solution of sebacoyl chloride in carbon tetrachloride a rapid reaction took place, but a good protective skin was not formed. The following combinations were studied as film forming reactions at a stationary interface. Epon 820 and 828 with tributyl amine, polyamide resin/heptane, N-methyl morpholine, trimethylamine/heptane and toluene diisocyanate; Polyol

10

G-2140 and toluene-diisocyanate; ethylene diamine and toluene diiso-
cyanate.

Triethylene tetramine was encapsulated using a sebacoyl chloride-
n-hexane silicone oil No. 200 system. In this case, a crosslinked poly-
meric skin was formed which was rigid enough to isolate. Analysis
indicated an 80% amine content. The amine was held long enough to
render some kind of wall post treatment very promising. Hydrazine
and a small amount of triethylene tetramine were tried with this system,
but empty capsule shells were obtained.

E. Summary and Conclusions

Initial permeability measurements indicated that
polymers from diamines and diacid chlorides were rather permeable
to small polar molecules even though interfacial polycondensation of
diamines and diacid chlorides offered a promising approach to encap-
sulation of high energy liquid fuels. The permeability of the polymer
film could possibly be lowered by subsequent modification of the film
or by depositing a secondary film around the original capsule.

It is felt that the permeability might also be lowered by a poly-
meric material approaching a hydrocarbon type backbone formed by
vinyl polymerization. The severe reaction conditions required for
such reactions would render polymerization in situ improbable. This
difficulty might be overcome by a two stage polymerization process.
Stage one would involve the preparation of a soluble high molecular
weight prepolymer containing active sites capable of further polymeri-
zation. This prepolymer may then be deposited around an internal

phase by some type of phase separation. Stage two would then consist of reinforcing the resulting capsular wall by further polymerizing the remaining active sites.

In conclusion the encapsulation of hydrazine or any reactive compound is indeed complex. One of the goals of the ONR endeavor was to obtain basic information and concepts which might help to solve this problem. It is believed that in this respect this secondary goal was accomplished.

What is sorely needed in the area of hydrazine encapsulation is a wall material, formed either in situ or by deposition, that is mechanically rigid and retains hydrazine long enough to render isolation and post treatment possible. At this point it is believed that hydrazine cannot be retained indefinitely without some type of post treatment. Post treatment might be achieved by depositing a second polymer around the initially formed polymeric skin and also might be further enhanced by cross-linking the second coating by a two stage polymerization process already discusses. Another possibility is to graft polymerize a second coat by catalytically forming an active site on the initial polymeric skin.

INTERIM REPORT NO. 5

In the further search for a wall material and encapsulation system that could be effectively utilized with high energy liquid fuels a number of polymers were prepared. In certain cases attempts were made to prepare capsules using these polymers as wall materials. The emphasis of this work was on the synthesis of soluble prepolymers containing an active site from difunctional monomers, the mechanism by which one site would preferentially polymerize leaving the other unreacted, the possible application of phase separation methods for depotition of these prepolymers around an internal phase and the mode of crosslinking these prepolymers.

A.   Polymer Studies

    1.   Prepolymers Based on Glycidyl Methacrylate

        a.   Cationic Polymerization of Glycidyl Methacrylate

            Glycidyl methacrylate was polymerized cationically by opening of the epoxy groups using boron trifluoride etherate as a catalyst to give a linear methanol soluble polymer containing residual methacrylic double bonds. Acetone soluble and acetone insoluble residues were obtained. Both residues were soluble in methanol. Infrared analysis showed that the acetone insoluble residue contained methacrylic double bonds and no epoxy groups and the acetone soluble residue contained epoxy groups but no unsaturations (trace if any).

$$n \; CH_2\text{-}CH \; CH_2\text{-}O\overset{\overset{O}{\|}}{C}\text{-}\underset{CH_3}{C}\text{=}CH_2 \quad \xrightarrow[\;0^0\,C.\;]{BF_3\text{-}O(ET)_2} \quad \left[\begin{array}{c} \text{-O } CH_2\text{-}CH\text{-} \\ CH_2 \\ O \\ CH_2 = C\text{-}C\text{=}O \\ CH_3 \end{array} \right]_n \; \begin{array}{l} +(I\text{-}6) \\ \text{Acetone} \\ \text{soluble} \end{array}$$

<div align="center">

(I-7)

Acetone insoluble
</div>
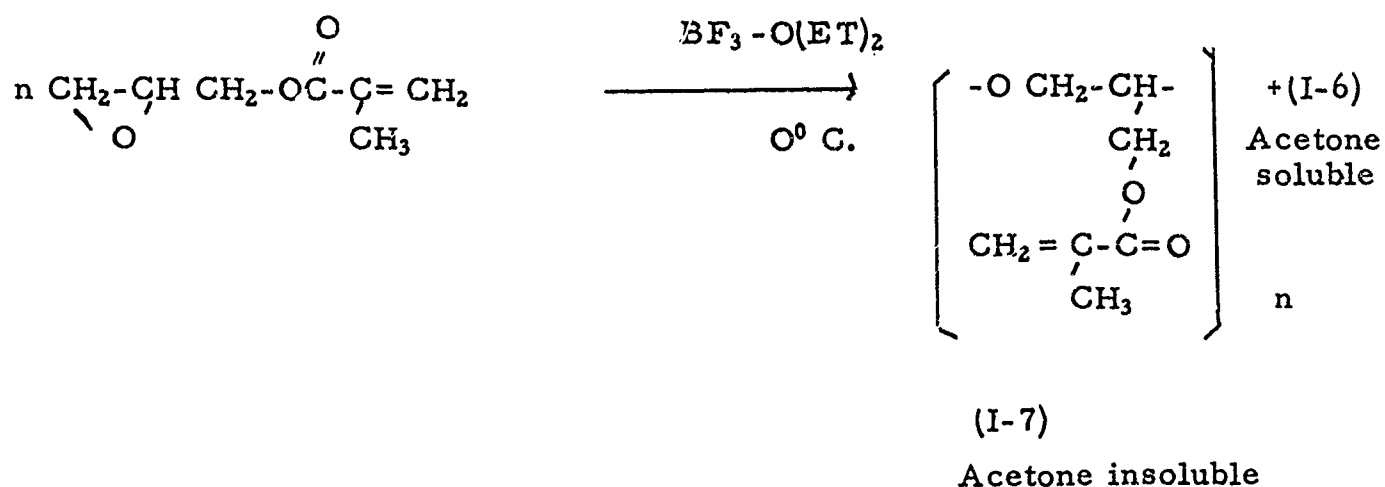
Through out this report the roman numerals will be used to desig-
nate a product and the arabic numerals (when used) will designate the
infrared spectrum number given in the appendix.

Compounds (I-7) and (I-6) are both viscous gums and the last of
a series of ten attempts to obtain a prepolymer with a high enough mole-
cular weight for the purpose of obtaining a powder which would deposit
a non tacky film from solution. In all cases gums were obtained.
Compound (I-7) gave a gel which was insoluble in methanol upon expo-
sure to a Gates ultra violet source for thirty minutes in the presence
of o - tolyldesyl sulfide (OTDS a photo initiator) indicating crosslinking
of the methacrylic double bond. Compound (I-6) did not gel after one
hour exposure.

Attempts to determine the amount of free hydroxy end groups by
the pyridine-acetic anhydride method in previous batches of the cationic
polymerization product did not give reproducible results. Fractions of
the samples were insoluble in the reagent and increasing the amount of
reagent dissolved more, but not all of the samples giving variable
results.

b. Free Radical Polymerization of Glycidyl Methacrylate

Glycidyl methacrylate has been polymerized by a benzoyl peroxide initiated free radical mechanism to give a linear soluble prepolymer containing epoxy side chains.

$$n\ CH_2 = \underset{CH_3}{\overset{}{C}} - \overset{\overset{O}{\parallel}}{C} - OCH_2 - CH - CH_2 \xrightarrow[80.^{0}C]{Bz_2O_2} \left[\begin{array}{c} CH_3 \\ - CH_2 - C - \\ C = O \\ CH_2 - CH - CH_2 - O \\ O \end{array} \right]_n$$

(II-3)
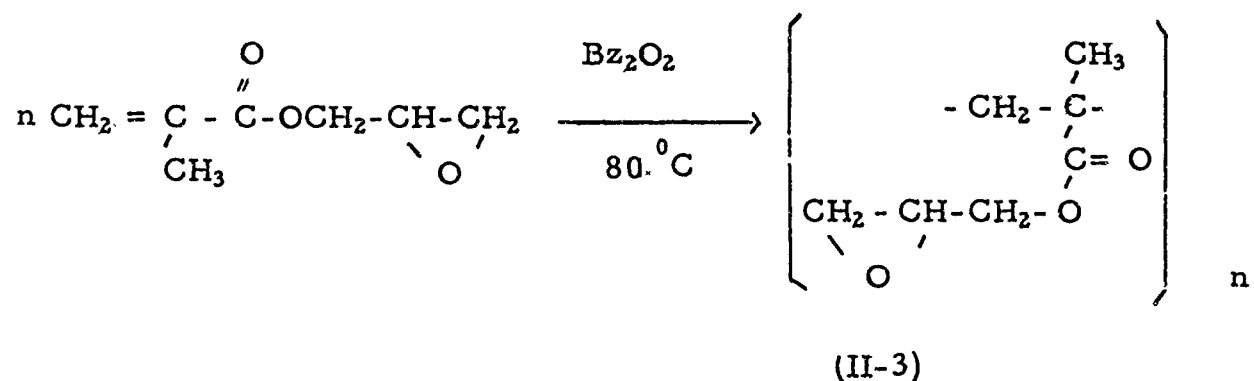
white powder

Infrared analysis showed that the methacrylic double bond has polymerized and the epoxy groups have remained unchanged. A non tacky film of this polymer could be cast from solution. When a few drops of boron trifluoride etherate was added to a 20% benzene solution of the polymer, a gel formed immediately. The polymer can also be cured by amines or heat. Analysis of the epoxy groups using the pyridine-HCl method gave a value of 6.41 milli equivalents of epoxy group per gram of sample. This corresponds to 27.6% epoxy groups in the polymer (% theory is 30.3).

2. Prepolymers Based on 2-Vinyloxyethyl Methacrylate

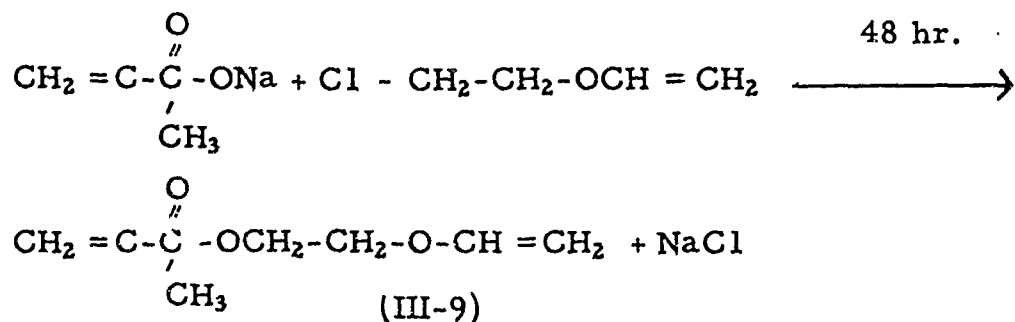a. Preparation of 2-Vinyloxyethyl Methacrylate

Since vinyl ethers are highly reactive in low temperature cationic addition polymerizations and methacrylates are quite reactive toward free radical addition polymerization, incorporation of these two functional groups into one monomer should render a two

-15-

stage polymerization process highly probable.

An early attempt was made to prepare 2-vinyloxyethyl methacrylate by coupling vinyl-2-iodoethyl ether with silver methacrylate. Since the iodoether was not commercially available, it was prepared by treating the chloroether with sodium iodide in acetone. Infrared analysis, vapor, phase gas chromatography and carbon, hydrogen, iodine analysis confirmed that the desired product was obtained.

$$CH_2 = CH - O-CH_2 \ CH_2 - Cl + NaI \xrightarrow{\quad Acetone \quad}$$

$$CH_2 = CH - OCH_2 \ CH_2 - I + Na \ Cl$$
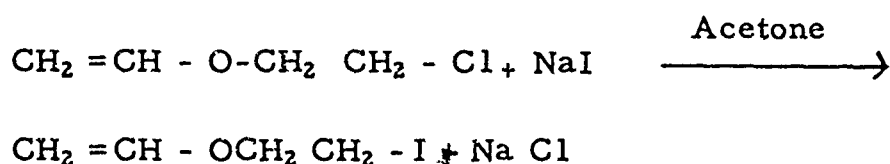
The reaction of silver methacrylate with the iodoether where the silver salt was dispersed in ether, however, was unsuccessful. When vinyl - 2 - chloroethyl ether was treated with sodium methacrylate and refluxed in acetonitrile, 2 - vinyloxyethyl methacrylate was obtained.

$$CH_2 = C-\overset{\overset{O}{\|}}{C}-ONa + Cl - CH_2-CH_2-OCH = CH_2 \xrightarrow{\quad 48 \ hr. \quad}$$
$$\underset{CH_3}{|}$$

$$CH_2 = C-\overset{\overset{O}{\|}}{C}-OCH_2-CH_2-O-CH = CH_2 + NaCl$$
$$\underset{CH_3}{|} \qquad (III-9)$$

Infrared analysis showed the presence of a vinyloxy double bond and a methacrylic double bond. Vapor phase gas chromatography showed only one product. Carbon hydrogen analysis was in agreement with structure given. Compound (III-9) reacts vigorously with boron trifluoride etherate at room temperature with charring.

-16-

b. Cationic Polymerization of 2-Vinyloxyethyl Methacrylate

2-Vinyloxyethyl methacrylate was polymerized cationically at low temperatures with Lewis acids by addition to the vinyloxy double bond to give a linear soluble prepolymer containing residual methacrylic double bonds.

$$n\ CH_2 = CH-O-CH_2-CH_2-O-\overset{\overset{O}{\underset{\|}{}}}{C}-\underset{\underset{CH_3}{|}}{C} = CH_2 \longrightarrow
\left[
\begin{array}{c}
-CH_2 - \underset{\underset{\underset{\underset{\underset{CH_2}{|}}{\underset{\underset{CH_2 = \overset{O}{\underset{\|}{C}} - \overset{}{\underset{\underset{CH_3}{|}}{C}} -O- CH_2}{}}{O}}}{O}}{CH} -
\end{array}
\right]_n$$
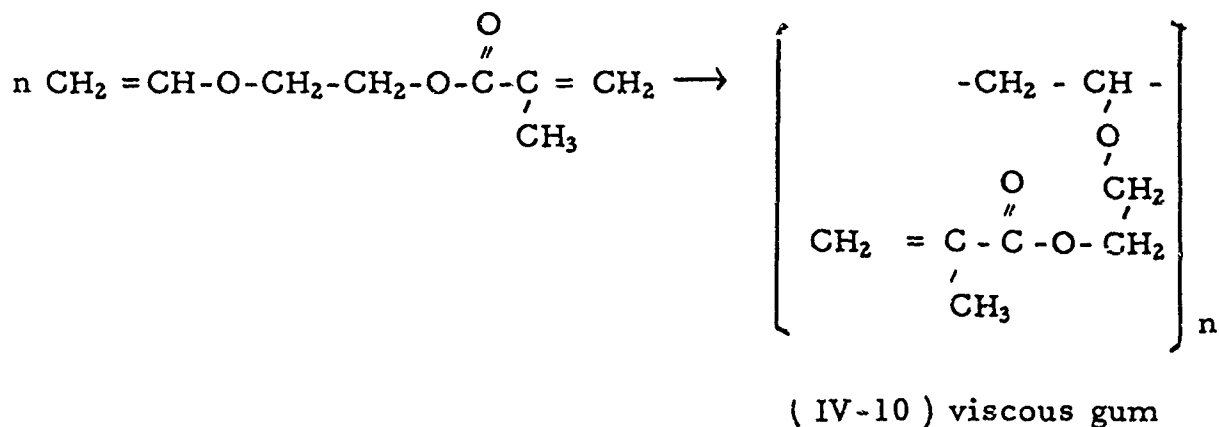
(IV-10) viscous gum

At first the reaction was carried out at O^0 C. using stannic chloride as the catalyst and a viscous gum was obtained. The reaction was carried out again at 60^0C. using boron trifluoride etherate as a catalyst in an attempt to increase the molecular weight in order to obtain a solid soluble prepolymer capable of depositing a non tacky film solution. A viscous gum was obtained in this case also. Infrared analysis showed in both cases that the vinyloxy double bond disappeared and a residual methacrylic double bond was still present. When (IV-10) which is soluble in methylene chloride was exposed to a Gates ultra violet source for 90 sec. in the presence of OTDS, a gel was formed. This gel was no longer soluble in methylene chloride indicating that free radical cross-linking through the methacrylic groups occurred.

-17-

c. Cationic Copolymerization of Styrene and 2-Vinyloxyethyl Methacrylate

A further attempt was made to obtain a polymer from 2-vinyloxyethyl methacrylate which could be deposited from solution to give a non tacky film. In this case, a 10: 1 styrene-2-vinyloxyethyl methacrylate copolymer was prepared by a cationic polymerization mechanism. If no homopolymerization occurred, the reaction can be represented ideally as follows:

$$n \ CH_2 = CHO-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{}{C}} = CH_2 + 10n \ CH_2 = \underset{C_6H_5}{\overset{}{CH}} \quad \xrightarrow[-60^0 \ C.]{BF_3 \ O(Et)_2}$$

$$\left[\begin{array}{c} -CH_2-CH- \\ O \\ CH_2 \\ O \qquad CH_2 \\ CH_2 = \overset{}{\underset{CH_3}{C}} - \overset{O}{\overset{\|}{C}}-O- \end{array} \right]_n \left[\begin{array}{c} CH_2-CH- \\ C_6H_5 \end{array} \right]_{10 \ n}$$
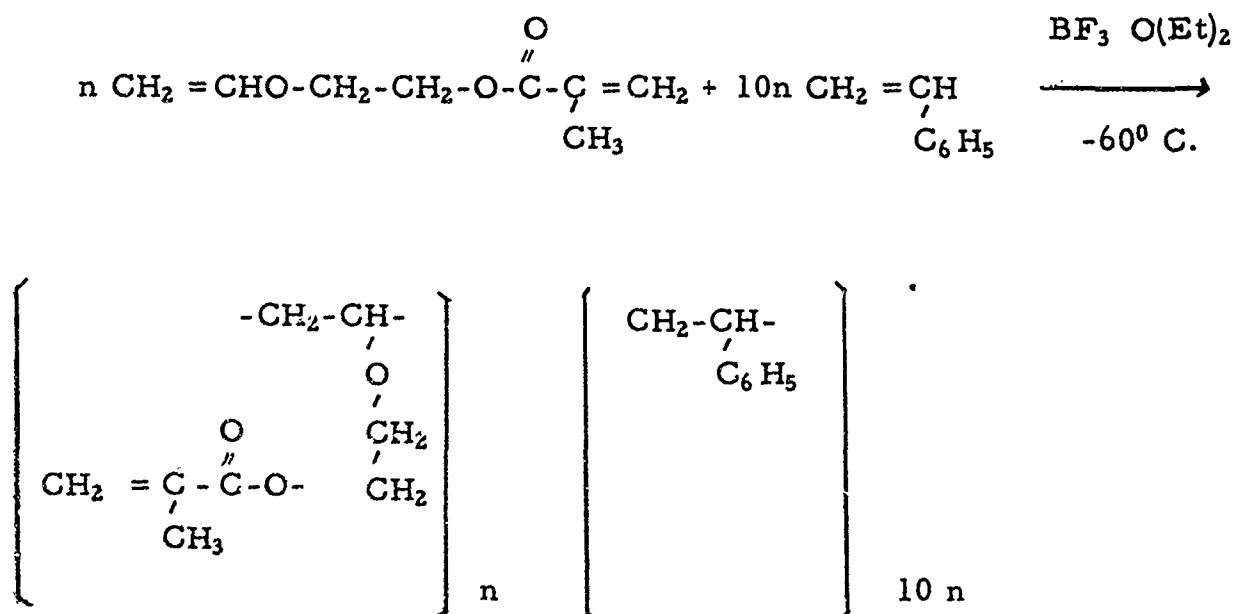
(V-11)

white powder

A white powder was obtained which could be deposited from solution as a dry non tacky film. Infrared analysis indicated that the vinyloxy double bond polymerized and that the methacrylic group was still present. A film of this copolymer deposited from a 20% methylene chloride solution containing a small amount of OTDS, when exposed to a Gates ultra violet source gave an insoluble film indicating crosslinking of the residual methacrylic groups.

3. **Prepolymers Based on 2-Hydroxyethyl Methacrylate**

   a. **Homopolymerization of 2-Hydroxyethyl Methacrylate**

The monomer 2-hydroxyethyl methacrylate was chosen for polymerization studies because polymers derived thereof would contain reactive hydroxygroups capable of further reaction. Unsaturation could also be introduced through the hydroxy function.
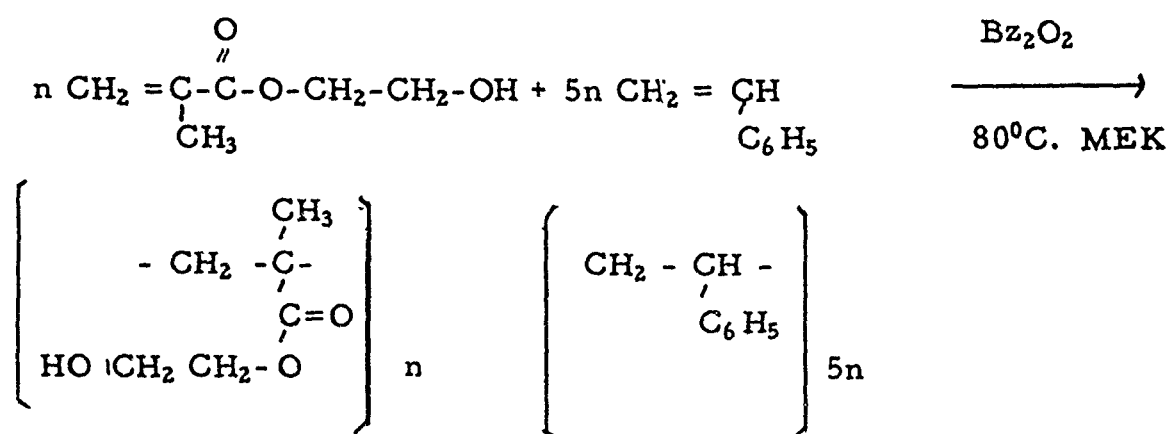
A free radical polymerization of 2-hydroxyethyl methacrylate dissolved in methyl ethyl ketone and initiated by azobisisobutyronitrile (A BIN) was attempted. It was hoped that a linear soluble polymer represented by the following reaction would be obtained.

$$n \; CH_2 = \underset{\underset{CH_3}{|}}{\overset{\overset{O}{||}}{C}} - C - O - CH_2 - CH_2 - OH \quad \xrightarrow[\text{MEK } 80^0 \text{ C.}]{\text{A BIN}} \quad \left[\begin{array}{c} CH_3 \\ | \\ CH_2 - C - \\ | \\ C = O \\ | \\ HO - CH_2 - CH_2O \end{array} \right]_n$$
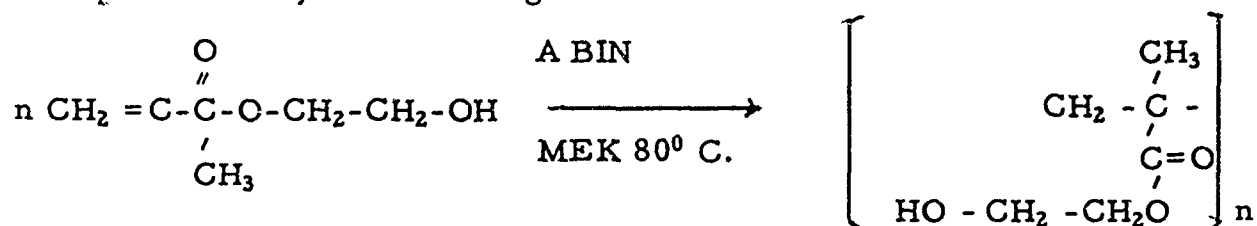
However, an insoluble swollen gel was formed. According to a Rohm and Haas bulletin., this monomer contains 1% ethylene glycol dimethacrylate formed by disproportionation of the monomer. This would be enough to cause gelation due to crosslinking.

   b. **Copolymerization of Styrene and 2-Hydroxyethyl Methacrylate**

The monomer 2-hydroxyethyl methacrylate was diluted with styrene in order to reduce the possibility of gelatin due to the presence of a small amount of ethylene glycol dimethacrylate, thereby making it possible to obtain a soluble linear copolymer containing the hydroxy function.

$$n \; CH_2 = \underset{\underset{CH_3}{|}}{C} - \overset{\overset{O}{\|}}{C} - O - CH_2 - CH_2 - OH \; + \; 5n \; CH_2 = \underset{\underset{C_6H_5}{|}}{CH} \quad \xrightarrow[80^{\circ}C. \; MEK]{Bz_2O_2}$$

$$\left[\begin{array}{c} \overset{\overset{CH_3}{|}}{-CH_2 - C -} \\ \underset{|}{C=O} \\ HO \; CH_2 \; CH_2 - O \end{array} \right]_n \quad \left[\begin{array}{c} CH_2 - CH - \\ \underset{|}{C_6H_5} \end{array} \right]_{5n}$$
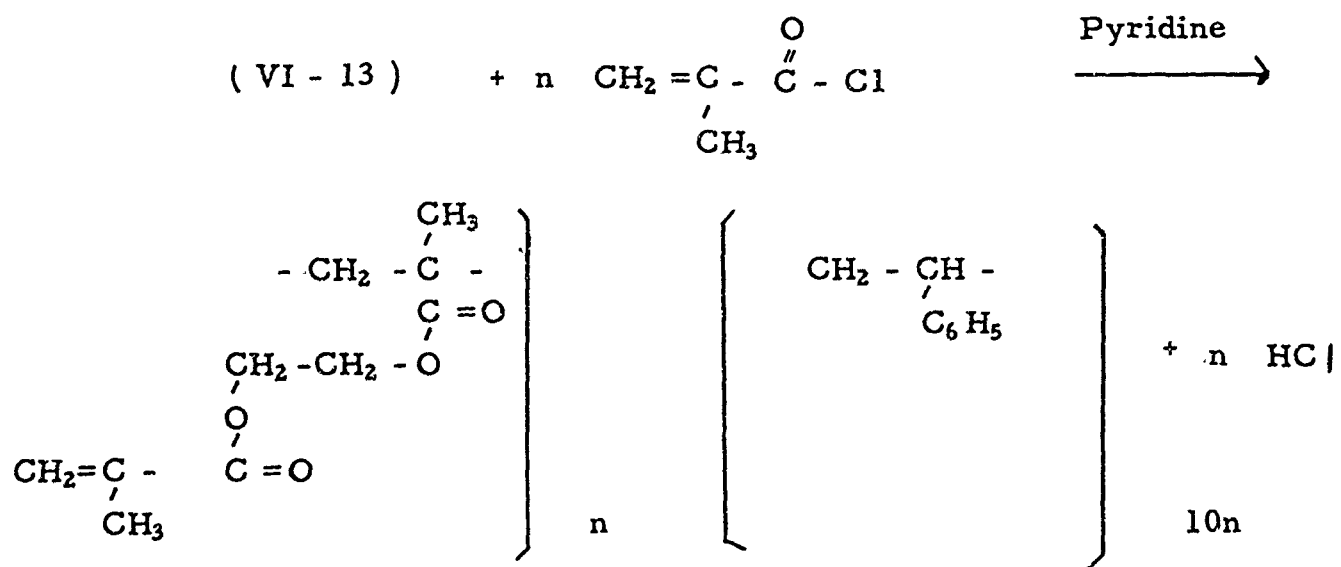
(VII - 15)

white powder

A linear soluble copolymer was also obtained here. Infrared analysis also indicated the presence of the hydroxy function (in greater amount relative to the carbonyl peak than (VI - 13) and the absence of vinyl unsaturation.

c. <u>Methacrylation of Styrene - 2-Hydroxyethyl Methacrylate Copolymers</u>

A methacrylic double bond was introduced into Copolymer (VI-13) by reaction with methacrylyl chloride.

$$(VI - 13) \quad + \; n \;\; CH_2 = \underset{\underset{CH_3}{|}}{C} - \overset{\overset{O}{\|}}{C} - Cl \quad \xrightarrow{\text{Pyridine}}$$

$$\left[\begin{array}{c} \overset{\overset{CH_3}{|}}{-CH_2 - C -} \\ \underset{|}{C=O} \\ CH_2 - CH_2 - O \\ \underset{|}{O} \\ CH_2 = \underset{\underset{CH_3}{|}}{C} - \quad C = O \end{array} \right]_n \quad \left[\begin{array}{c} CH_2 - CH - \\ \underset{|}{C_6H_5} \end{array} \right]_{10n} \quad + \; n \;\; HCl$$
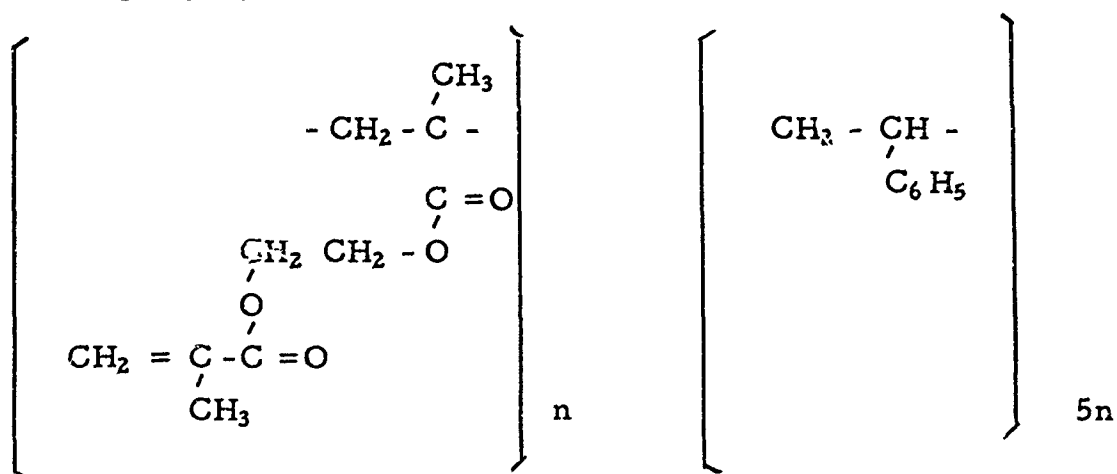
(VIII - 14)

white powder

-21-

A linear soluble copolymer was obtained which could be deposited as a non tacky film from solution. Infrared analysis indicated the introduction of a methacrylic double bond and the disappearance of the hydroxy groups. A film when exposed to a Gates ultra violet source in the presence of OTDS became insoluble indicating that crosslinking had occurred.

In a similar way Copolymer (VII - 15) was methacrylated to give the following copolymer:

$$
\left[
\begin{array}{c}
CH_3 \\
\diagup \\
-CH_2-C- \\
C=O \\
\diagup \\
CH_2\ CH_2-O \\
\diagup \\
O \\
\diagup \\
CH_2=C-C=O \\
\diagup \\
CH_3
\end{array}
\right]_n
\left[
\begin{array}{c}
CH_2-CH- \\
\diagup \\
C_6H_5
\end{array}
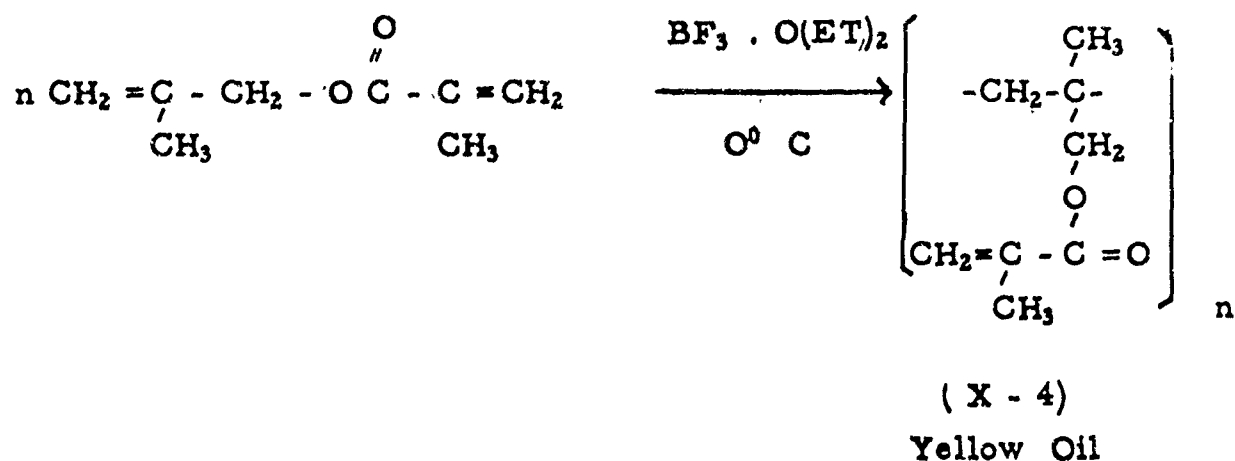\right]_{5n}
$$

(IX - 16)

White Powder

Again a linear soluble copolymer was obtained which could be deposited as a non tacky film from solution. Infrared analysis indicated the introductions of a methacrylic double bond (in greater amount relative to the carbonyl peak than (VIII - 14)) and the disappearance of the hydroxy group. A film of copolymer (IX - 16) could also be photocrosslinked.

4. Prepolymer Based on Methallyl Methacrylate

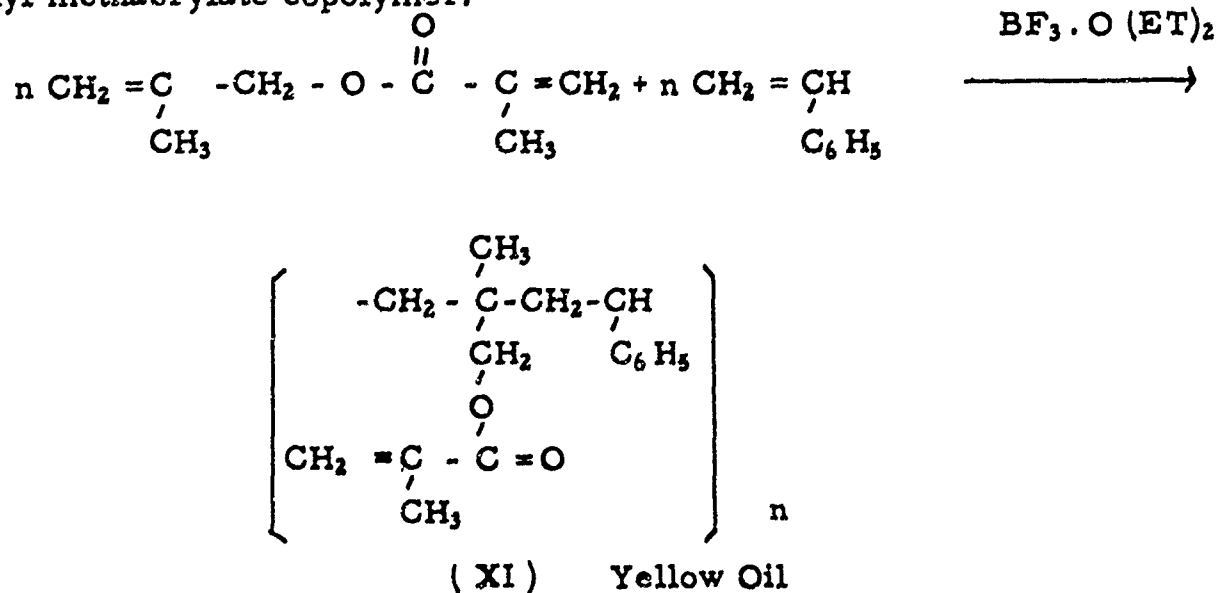a. Attempted Cationic Polymerization of Methallyl Methacrylate

-22-

A cationic polymerization of methallyl methacrylate catalyzed by boron trifluoride etherate was attempted in order to prepare a prepolymer formed through the methallyl linkages while retaining the methacrylic double bond.

$$n\ CH_2 = \underset{CH_3}{C} - CH_2 - O\ \overset{O}{\overset{\|}{C}} - \underset{CH_3}{C} = CH_2 \quad \xrightarrow[\text{0}^0\ C]{BF_3\ .\ O(ET)_2} \quad \left[\begin{array}{c} CH_3 \\ | \\ -CH_2 - C - \\ | \\ CH_2 \\ | \\ O \\ | \\ CH_2 = \underset{CH_3}{C} - C = O \end{array} \right]_n$$

(X - 4)

Yellow Oil

Infrared analysis, however, indicated that (X-4) was identical with the methallyl methacrylate (see spectrum No. 5). Therefore, either no prepolymer or a very low molecular weight prepolymer was obtained.

b. **Attempted Cationic Copolymerization of Methallyl-**
   Methacrylate with Styrene

A further attempt was made to polymerize methallyl methacrylate cationically and in this case as a 1: 1 styrene methallyl methacrylate copolymer.

$$n\ CH_2 = \underset{CH_3}{C}\ -CH_2 - O - \overset{O}{\overset{\|}{C}} - \underset{CH_3}{C} = CH_2 + n\ CH_2 = \underset{C_6H_5}{CH} \quad \xrightarrow{BF_3\ .\ O\ (ET)_2}$$

$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2 - \underset{\underset{O}{\overset{|}{\underset{|}{CH_2}}}}{C} - CH_2 - \underset{C_6H_5}{CH} \\ | \\ CH_2 = \underset{CH_3}{C} - C = O \end{array} \right]_n$$
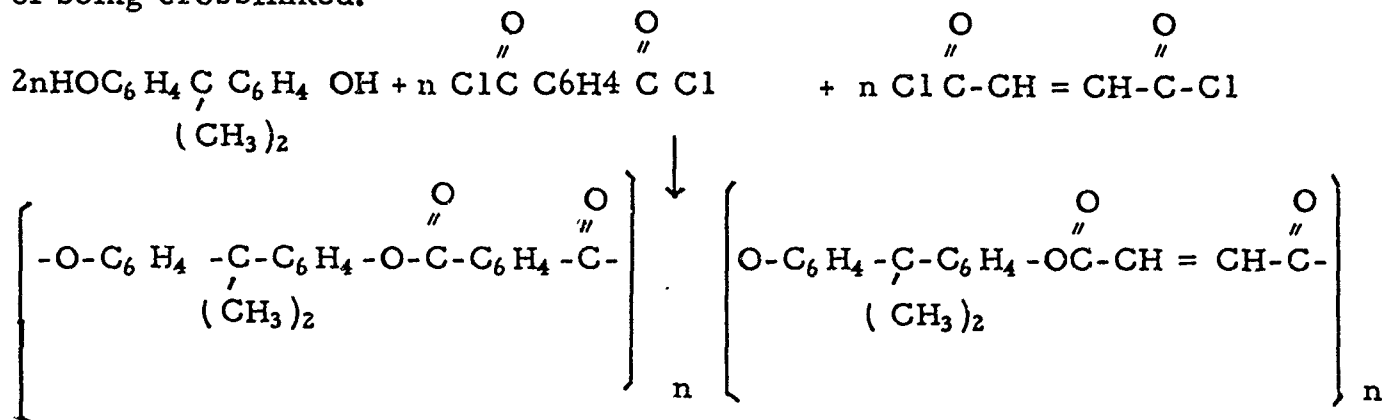
(XI)   Yellow Oil

-23-

Infrared analysis indicated that (Xl), a yellow oil was mostly a mixture

of styrene and methallyl methacrylate and/or low molecular weight

copolymer. No further work was attempted with this series of mono-

mers.

5. Prepolymer from Interfacial Polycondensation
    Product

a. Interfacial Polycondensation of Bisphenol A
    with 1:1 mixture of Terephthaloyl and Fumaroyl
    Chloride

A condensation copolymer was prepared by

interfacial polymerization from bisphenol A and a 1:1 mixture of tereph-

thaloyl and fumaroyl chloride to give a linear soluble prepolymer capable

of being crosslinked.

$$2nHOC_6H_4 \underset{(CH_3)_2}{C} C_6H_4 OH + n\ ClC\ C6H4\ C\ Cl \quad + n\ Cl\ C-CH=CH-C-Cl$$

$$\left[-O-C_6H_4 \underset{(CH_3)_2}{-C} -C_6H_4 -O-C-C_6H_4 -C- \right]_n \cdot \left[O-C_6H_4 \underset{(CH_3)_2}{-C} -C_6H_4 -OC-CH=CH-C- \right]_n$$

(XII)

White Powder

A film of (XII) deposited from a methylene chloride solution and after

exposure to a Gates ultra violet source in the presence OTDS became in-

soluble. An attempt was made to prepare a free film so that the amount

of water permeation through the uncrosslinked and crosslined film might

be compared. However, a very brittle film was obtained which would not

hold together on handling.

6. Synthesis

    a. Cationic Polymerization of Glycidyl Methacrylate (1-7)

Quantities used:

50g. glycidyl methacrylate in 200 ml. methylene chloride.

0.025 g. hydroquinone (free radical inhibitor)

5.6 g. boron trifluoride etherate.

In a 500 ml. resin glask equipped with a mechanical stirrer and drying tube were placed 50 g. glycidyl methacrylate in 200 ml. of methylene chloride and 0.025 g. of hydroquinone. The solution was cooled in an ice bath and 5.6 g. boron trifluoride etherate was added in portions. The reaction was continued for 4 hrs. A white slurry was formed which dissolved upon the addition of 25 ml. methanol. The solution was allowed to warm to room temperature and 75 ml. of 50% K_2CO_3 was added and the resulting mixture shaken well in a sepratory funnel. The upper organic layer was separated. The lower layer was washed with methanol and the methanol washings combined with the organic layer. The organic layer (methanol solution) was dried over K_2CO_3 and the solvent removed. Acetone (100 ml.) was added to the residue and two layers formed. The upper acetone layer was dried and the solvent removed. A reddish brown gum was obtained (1-6). Infrared analysis indicated that epoxy groups were present, but no methacrylic double bond (trace if any). The lower acetone insoluble layer was dried and stripped and a reddish gum was obtained (1-7). Infrared an 'ysis indicated that the epoxy group polymerized and the methacrylic double bond was still present.

b.   Preparation of Vinyl Homopolymer of Glycidyl
       Methacrylate [3]

(II-3)

Quantities used:

50 g. (0.35M) glycidyl methacrylate in 250 ml. methyl
ethyl ketone

0.5 g. (1% based on monomer) benzoyl peroxide

In a 500 ml. three necked glask equipped with a mecha-
nical stirrer, gas inlet tube and reflex condenser were placed 50g. gly-
cidyl methacrylate 250 ml. methyl ethyl ketone and 0.5g. benzoyl pero-
xide. The solution was heated to reflex at 80^{0}C. under a nitrogen
blanket for 4 hrs. and allowed to cool. To a Waring blender was added
300 ml. of isopropyl alcohol and to this the polymer solution was added
dropwise while stirring vigorously. The white precipitate which formed
was filtered, washed and dried. A white powder (II-3) (33g., 67%) was
obtained. Infrared analysis indicated that the methacrylic double bond
disappeared and the epoxy group was still present.

Epoxy group found: 27.6%; calcd. 30.3%

c.   Preparation of Vinyl 2-Iodoethyl Ether

Quantities used:

64g. (0.6M) vinyl-2-chloroethyl ether
a trace of hydroquinone

113g. (0.75M) sodium iodide in 200 ml. dry acetone.

A three necked flask equipped with a mechanical stirrer,
drying tube and a reflux condenser was charged with 64 g. of vinyl-2-
chloroethyl ether, 113 g. of sodium iodide a trace of hydroquinone and
200 ml. of dry acetone. The resulting mixture was heated to reflux in

a silicone oil bath for 24 hr. The salt which precipitated was filtered

off, washed with acetone, dried and weighed. The amount of sodium

chloride obtained (25.4g.) correspond to a 72% yield (did this to check

extent of reaction). The organic filtrate was evaporated to remove most

of the acetone. Water (500 ml.) was added to the organic residue and

the salt which was just precipitated was added to help phase out the

organic layer. The organic and aqueous layers were separated and

the organic layer was washed with 100 ml. 5% sodium bisulfite solution

(to prevent oxidation of the iodo ether). The aqueous layer was washed

with 100 ml. of chloroform and the organic layers combined and dried.

The solvents were removed by distillation at atmospheric pressure. The

product was fractionated by vacuum distillation and a fraction b.p. 48-

50°C/16 mm was collected. The product 28.6g. was a light yellow liquid

$n_D^{28} = 1.5209$. Refractive index of the chloroether $n_D^{28} = 1.4324$. Vapor

phase gas chromatography indicated the product to be distinct from the

starting chloroether. Infrared analysis showed a vinyloxy double bond

and no chlorine peak. Analysis Found:

C, 24.6; H, 3.80; I, 63.9. Calcd., C, 24.3; H, 3.56; I, 64.1.

        d.   <u>Reaction of Vinyl-2-Iodoethyl Ether with Silver</u>
<u>Methacrylate</u>

        Quantities used:

        8.9g. silver methacrylate (0.046M) suspended in
100 ml. ether.

        9.8g. vinyl-2-iodoethyl ether (0.0495M).

        Trace of copper powder and hydroquinone (inhibitors).

Silver methacrylate was prepared by the action of silver nitrate on sodium methacrylate. A three necked flask equipped with a mechanical stirrer, reflux condenser and drying tube was charged with 8.9g. fo silver methacrylate suspended in 100 ml. of ether, 9.8 g. of vinyl-2-iodoethyl ether and a trace of copper powder and hydroquinone. The reaction mixture was heated to reflux for 72 hr. The precipitate was filtered and the resulting green filtrate solution (coloration could not be removed with charcoal) was washed with water and separated. The ether was removed and the organic residue dried and vacuum distilled. The bulk of the product was collected at b.p. 48-49°C/16mm and a light yellow liquid was obtained. $n_D^{28.8}$ = 1.5119. Vapor phase gas chromatography and infrared analysis indicated that the bulk of the product was the starting iodo compound.

e. Preparation of 2-Vinyloxyethyl Methacrylate (III-9)

Quantities used:

34g. (0.32M) vinyl-2-chloroethyl ether dissolved in 50 ml. acetonitrile.

40g. sodium methacrylate (0.37M) in 150 ml. acetonitrile.

0.5g. benzyltrimethyl ammonium chloride (0.8g. of a 60% aqueous solution).

0.2 hydroquinone (inhibitor).

A three necked flask equipped with a mechanical stirrer, dropping funnel and reflux condenser was charged with 40g. of sodium methacrylate in 150 ml. acetonitrile, 0.5g. of benzyltrimethyl ammonium chloride catalyst and 0.2g. of hydroquinone and the mixture heated to reflux. Vinyl-2-chloroethyl ether (34g.) in 50 ml. of acetonitrile was then added dropwise to the refluxing mixture and the reaction was allowed to proceed at

reflux for 48 hr. The precipitate was filtered off and the organic filtrate distilled at atmospheric pressure to remove most of the acetonitrile. The organic residue was vacuum distilled and a fraction collected at b.p. 75-83°C/15mm., (20g. 40% crude). This fraction was redistilled and the chloroether was collected at b.p. 57-61°C/90mm. The product (15g. (III-9)) was collected at 82-83°C/15mm., n_D^{25} =1.4609, n_D^{20} lit[4] =1.4469, b.p. lit[4] =76°C/10mm. The product was confirmed by infrared analysis which showed the presence of both a vinyl oxy and methacrylic double bond. Vapor phase gas chromatography showed only one compound present. Analysis Calcd. for $C_8 C_{12} O_3$: C, 61.5; H, 7.7. Found C, 61.66, 61.43; H, 7.71, 7.72. The product reacted vigorously with $BF_3 . O (Et)_2$.

f. Preparation of Cationic Polymerization Product of 2-Vinyloxyethyl Methacrylate (IV-10).

Quantities used:

5g. 2-vinyloxyethyl methacrylate (III-9).

0.25g. (5% based on monomer) of freshly distilled boron trifluoride etherate.

A jacketed three necked resin flask equipped with a mechanical stirrer, dropping funnel and drying tube was charged with 50 ml. of methylene chloride. This was cooled to -60°C. by pumping dry ice acetone bath fluid through the jacketed flask. Boron trifluoride etherate 0.05g. was then added followed by addition of 5g. of 2-vinyloxyethyl methacrylate through the dropping funnel. When all of the monomer was added an additional 0.2g. of boron trifluoride etherate was added. Stirring was continued at 60°C for 4 hr. After the reaction temperature warmed up to -30°C, 25 ml. of a 1% solution sodium hydroxide was added and the reaction mixture was allowed to warm to room temperature while

-29-

stirring. The methylene chloride layer was separated, washed with water, dried and the volitile components removed at 50°C. /.3mm. A light yellow viscous gum (3.4g. 68%) was obtained (IV-10). Infrared analysis indicated that the vinyloxy group polymerized and the methacrylic double bond was still present. This polymerization was also carried out at 0°C. using stannic chloride as a catalyst giving identical results.

g. Preparation of 10: 1 Styrene - 2-Vinyloxyethyl Methacrylate Copolymer (V-11)

Quantities used:

1.5g. 2-vinyloxyethyl methacrylate (0.0096M (III-9)).

9.98g. styrene (0.096M).

0.55g. boron trifluoride etherate (5% based on total monomers).

A jacketed resin flask equipped with a mechanical stirrer and drying tube was charged with 50 ml. methylene chloride, 1.5g. 2-vinyloxyethyl methacrylate (III-9) and 9.8g. styrene. The reaction solution was cooled to -60°C. and to this was added in three portions 0.55g. boron trifluoride etherate. After 4 hr. the temperature was allowed to warm to -10°C. and 25 ml. of a 1% solution sodium hydroxide solution was then added. After warming to room temperature the methylene chloride layer was separated and dried. The copolymer was precipitated by adding the methylene chloride solution slowly to 150 ml. of methanol while stirring in a Waring blender. The product was filtered washed with methanol and dried in a vacuum oven. A white powder 7g. (61% V-11) was obtained. Infrared analysis indicated that the copolymer still contained a methacrylic double bond. A non tacky film of this copolymer could be deposited

from solution.

h. Homopolymerization of 2-Hydroxyethyl Methacrylate

Quantities used:

50g. of 2-hydroxyethyl methacrylate.

0.5g. azobisisobutyronitrile (1% based on monomer)

A 500 ml. resin flask equipped with a mechanical
stirrer, gas inlet tube, reflux condenser and dropp-
ing funnel was charged with 250 ml. of methyl ethyl ketone and this was
heated to reflux under a nitrogen blanket. To this was added dropwise
a solution of 50g. of 2-hydroxyethyl methacrylate and 0.5g. azobisisobu-
tyronitrile followed by 50 ml. of methyl ethyl ketone. The reaction
solution was refluxed at 80°C. for 4 hr. A swollen insoluble gel was
formed. Attempts to isolate the gel in the form of a soluble powder were
unsuccessful.

i. Preparation of 10:1 Styrene -2-Hydroxyethyl
Methacrylate Copolymer (VI-13)

Quantities used:

50g. (0.48M) styrene.

6.2g. (0.048M) 2-hydroxyethyl methacrylate.

0.56g. of benzoyl peroxide (1% based on total
monomers).

A 500 ml. resin flask equipped with a reflux con-
denser mechanical stirrer, dropping funnel and a gas inlet tube was
charged with 250 ml. methyl ethyl ketone and heated to reflux under a
nitrogen blanket. To the refluxing solvent was slowly added through a
dropping funnel a solution of 50g. of styrene, 6.2g. of 2-hydroxyethyl
methacrylate. 0.56g. of benzoyl peroxide and 50 ml. of methyl ethyl

-31-

ketone. When addition of the monomers was complete the reaction was continued at 80°C. for 5 hr. The methyl ethyl ketone solution of the copolymer was added slowly to a methanol water solution in a Waring blender. A white tacky dough was obtained. This dough was filtered and dried in a vacuum oven and the brittle solid thus obtained was ground up with mortar and pestle and redried. A white powder (24g. (VI-13)) was obtained. Infrared analysis showed hydroxy and poly-styrene peaks.

j. Preparation of 5: 1 Styrene - 2 Hydroxyethyl Methacrylate Copolymer (VII-15)

Quantities used:

50g. (0.48M) styrene.

12.5g. (0.096M) 2-hydroxyethyl methacrylate.

0.63g. benzoyl peroxide (1% based on total monomers).

The procedure was the same as that used for the 10:1 copolymer (VI-13). A white powder (20g.)VII-15)) was obtained. Infrared analysis indicated that the hydroxy peak relative to the carbonyl peak is greater than the correspond 10:1 styrene -2-hydroxyethyl methacrylate copoly-mer (VI-13).

k. Methacrylation of 10:1 Styrene -2-Hydroxyethyl-Copolymer (VIII-14)

Quantities Used:

10g. (0.0085M) 10:1 styrene -2-hydroxyethyl metha-crylate copolymer (VI-13).

2g. (0.02M) methacrylyl chloride.

4mg. hydroquinone (0.2% based on acid chloride).

A 250 ml. resin flask equipped with a mechanical stirrer, reflux condenser, dropping funnel and drying

tube was charged with 10g. of 10:1 styrene -2-hydroxyethyl methacry-

late copolymer (VI-13), 90 ml. dry pyridine and 4mg. of hydroquinone. To this was added slowly 2g. of methacrylyl chloride at room temperature. After all the acid chloride was added, an additional 50 ml. of pyridine was added and the reaction heated to 50°C. for 4 hr. The reaction mixture was then diluted with 100 ml. of acetone and poured into a water in the Waring blender. A milky emulsion was obtained. The emulsion was broken up by the addition of a small quantity of 10% sodium hydroxide solution. The precipitate was filtered washed and dried and 9. 1g (86% (VIII-14) was obtained. The product could be deposited from solution as a non tacky film. Infrared analysis showed the introduction of the methacrylic double bond and the disappearance of the hydroxy group.

1. <u>Methacrylation of 5: 1 Styrene -2-Hydroxyethyl Methacrylate Copolymer (IX-16)</u>

Quantities Used:

10g. (0. 015M) 5: 1 styrene -2-hydroxyethyl methacrylate copolyme r (VII-15).

4g. (0. 04M) methacrylyl chloride.

8 mg. hydroquinone (0. 2% based on acid chloride).

The procedure was the same as that for the preparation of the 10: 1 copolymer (VIII-14) with the exception; instead of diluting with acetone, the reaction mixture was partially evaporated under vacuum to remove the excess acid chloride and pyridine. A white powder (10g. 93% (IX-16) was obtained. The product could be deposited from solution as a non tacky film. Infrared analysis showed the amount of methacrylic double bond relative to the carbonyl peak is greater than the corresponding 10: 1 copolymer (VIII-14).

m. Attempted Cationic Polymerization of Methallyl Methacrylate (X-4)

Quantities Used:

10g. methallyl methacrylate in 40 ml. methylene chloride.

2g. boron trifluoride etherate.

A resin flask equipped with a mechanical stirrer and drying tube was charged with 10g. of methallyl methacrylate and 40 ml. of methylene chloride. This solution was cooled in an ice bath and 2g. of boron trifluoride etherate was added in portions. The reaction was allowed to continue for 4 hr. at $0°C$. and then allowed to warm to room temperature over a period of 2 hr. The solution was washed with 25 ml. of 5% aqueous base and the methylene chloride layer separated. The aqueous layer was washed with 15 ml. of methylene chloride and the methylene chloride solutions combined and dried overnight. The methylene chloride was removed from the product under vacuum. A light yellow liquid (8g.) residue was obtained. Infrared analysis showed this liquid residue to be identical with the starting material (methallyl methacrylate). All of the liquid residue distills at $25°C/1mm$.

n. Attempted Cationic Copolymerization of 1:1 Styrene-Methallyl Methacrylate (XI)

Quantities used:

7g. (0.05M) methallyl methacrylate.

5.2g. (0.05M) styrene.

0.66 g. boron trifluoride etherate (1% based on total monomers).

A resin flask equipped with a mechanical stirrer and drying tube was charged with 7g. of methallyl methacrylate, 5.2g. of

styrene and 50 ml. of methylene chloride. The solution was cooled to -60°C. and to this was added 0.66 g. of boron trifluoride etherate in three portions. After 6 hr. the reaction was allowed to warm to 0°C. and the solution was washed with 25 ml. of 1% sodium hydroxide solution and the methylene chloride layer separated. The aqueous solution was washed with methylene chloride and the methylene chloride solutions combined and dried overnight. The methylene chloride was then evaporated under vacuum and the residue evaporated at 40°C/0.3 mm. Very little residue was left in the pot after this and 9. g. of light yellow oil was collected in the cold trap. Infrared analysis indicated that this light yellow oil was mostly a mixture of styrene and methallyl methacrylate and/or a low molecular weight copolymer.

o. Preparation of Copolymer from Bishphenol A and 1:1 Terephthaloyl and Fumaroyl Chloride. [5]

Quantities Used:

11.5 g. (0.05M) bisphenol A in 300 ml. of 0.1M sodium hydroxide solution.

3g. Duponol ME. in 30 ml. water.

5.1 g. (0.025M) terephthaloyl chloride and 3.8 g (0.025M) fumaroyl chloride in 150 ml. methylene chloride.

A solution of 11.5g. of bisphenol A and 4g. sodium hydroxide in 300 ml. of water was prepared by mixing in a Waring blender. A second solution was prepared containing 5.1g. of terephthaloyl chloride and 3.8g. of fumaroyl chloride in 150 ml. of methylene chloride. To the aqueous solution was added slowly a solution of 3g. of duponol ME. in 30 ml. of water. The organic acid chloride

solution was then added all at once to the aqueous solution in the Waring
blender and stirring was continued for 5 min. The resulting emulsion
was poured into 1500 ml. of acetone under vigorous stirring in order to
coagulate the copolymer. The copolymer was filtered, washed with
three 500 ml. portions of water, then acetone and dried in a vacuum
oven. A white powder (7g. 41% (XII)) was obtained. P.M.T. was about
260^0C. A 20% methylene chloride solution of this copolymer deposited
a very brittle film.

B.   Encapsulation Studies

This part of the report deals with the utilization of
interfacial polymerization and phase separation techniques in conjunc-
tion with the synthetic materials and ideas discussed in Part II towards
capsule wall formation.

1.   Study Using the Cationic Polymerication Product of
Glycidyl Methacrylate (I-7)

An attempt was made to encapsulate a water droplet
with the cationic polymerization product of glycidyl methacrylate (I-7)
by phase separation with subsequent free radical crosslinking of the
residual methacrylic side chains.

A 25 ml. water solution containing 2% (base of polymer)
of ammonium persulfate and 1% gum arabic was dispersed in 100 ml.
of a benzene solution containing 2.5% of dissolved polymer (I-7), 1% gum
demar No. 1 (based on water solution) and 1 drop of benzyl mercaptain.
To this stirring dispersion was added slowly 80 ml. n - hexane to phase
out the polymer. The resulting dispersion was heated to 60^0C. in a water
bath for 2 hr. and aliquots were examined microscopically at various

stages. A thin wall appeared to form around the droplets, but was not rigid enough to isolate by filtering through a fine sieve.

2. Studies Using the Vinyl Homopolymer of Glycidyl Methacrylate (II-3).

Studies were carried out in an attempt to deposit the vinyl homopolymer of glycidyl methacrylate (II-3) around an internal phase with subsequent crosslinking of the residual epoxy groups by curing with a Lewis acid or an amine.

a. Water Internal Phase - Boron Trifluoride Etherate Cure

A dispersion was prepared from 100 ml. of chloroform solution containing 3% polymer)II-3) and 25 ml. of water. To this stirring dispersion was added slowly 100 ml. of pet. ether (b. p. 30-60°C) for the purpose of phasing out the polymer around the water droplets. An irregular wall was formed. An attempt to cross-link the residual epoxy groups by the addition of 15 drops of boron tri-fluoride etherate resulted in rapid gelation and aggregation of the particles. No capsules could be isolated for identification.

b. Amine Internal Phase - Amine Cure

It was thought that perhaps an excess of an amine used in conjunction with an epoxy polymer might be used as both an internal phase and an epoxy wall curing agent.

Into 50 ml. of chloroform was dissolved 1.7 g of polymer (II-3). To this was added while stirring a mixture of an excess of 10g. triethylene tetramine with an initial amount of 50 ml. of silicone No. 200 to form a dispersion. The amine and the silicone

-37-

oil were added together because the amine alone would dissolve in the chloroform. A certain amount of polymer phases out in this step. The quantity of excess amine was calculated to give an 80% amine internal phase. An additional 50 ml. of silicone was slowly added to phase separate the polymer and stirring of the dispersion was continued for a few hours. The silicone oil is acting here as both a dispersion and phase separating medium. The supernatant liquid was decanted and the particles diluted with chloroform. Microscopic examination revealed irregular shaped gelled solids.

c. Water Internal Phase - Amine Cure

Polymer (II-3) 1.2g was dissolved in 50 ml. of chloroform and to this was added a small amount of span 85 and 50 ml. of water. The resulting mixture was stirred to form an emulsion. This emulsion was then added to 150 ml. of silicone oil No. 200 and stirred. The attempt made here was to form a double dispersion consisting of a water-chloroform dispersion, dispersed in silicone oil. It is not known whether water is dispersed in chloroform or chloroform is dispersed in water, however, photographs indicated that there was some kind of a double dispersion. To the double dispersion was added 2 g. of triethylene tetramine and the dispersion was allowed to stir for two days. Microscopic examination indicated that single and aggregate particles containing a wall were formed. This wall could be swelled by the addition of chloroform. The dispersion was diluted with n-hexane and the supernatant liquid decanted. Aggregates of rubbery particles were obtained. When these particles were diluted with chloroform, microscopic examination revealed upon the evaporation of chloroform, formation

-38-

of gel-like beads which finally collapsed on standing.

    d.   <u>Water-Amine Internal Phase - Amine Cure</u>

        In this case a dispersion was prepared by adding
50 ml. of a water solution containing 10 g of triethylene tetramine to
100 ml. of a chloroform solution containing 1.7 g of polymer)II-3). The
dispersion was allowed to stir overnight (n o silicone oil was used in
this case). Microscopic examination revealed irregular shaped partic-
les and indications of a very highly swelled thin gel-like wall (if any)
surrounding some of the droplets.

        This attempt resembles encapsulation by inter-
facial polymerization similar to the amine acid chloride type.   The
amine which is initially dissolved in the water phase partitions itself
between the water phase and the acid chloride containing organic phase.
As soon as the amine comes into contact with the acid chloride a rapid
reaction takes place in the organic phase forming a polymeric skin on
the organic side of the interface. The rate of transfer of the amine into
the organic phase is slow compared to the rate of polymerication. If
this were not so, the amine would have time to penetrate more deeply
into the acid chloride layer, and reaction and polymer precipitation
would take place more diffusely. [5]

        In the case of the amine epoxy reaction discussed
above, the rate of reaction may be too slow to render any appreciable
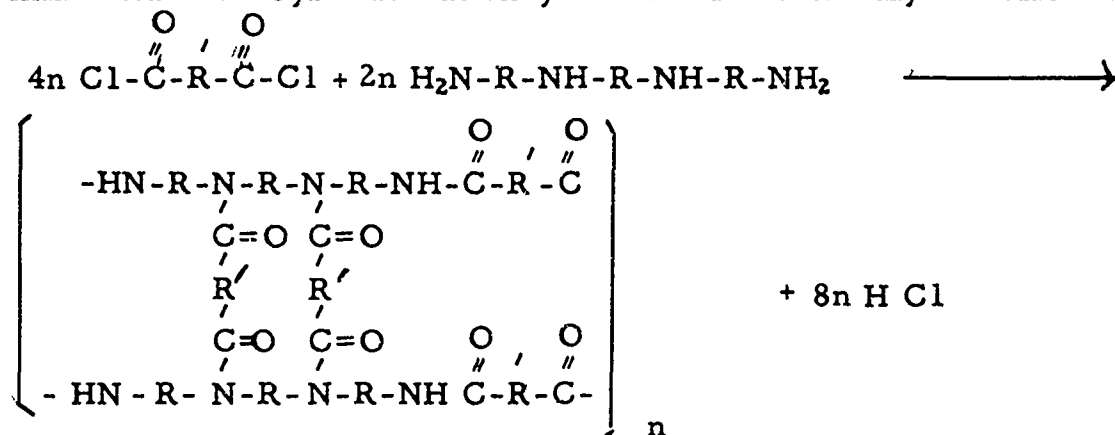interfacial skin forming reaction possible.   The attempt nevertheless
was made.

    3.   <u>Studies on Amine Encapsulation by Interfacial Polymeri-
zation</u>

        In the previous discussion it was pointed out that the

reaction of an epoxide with an amine in an interfacial polymerization
may be too slow for the formation of an interfacial polymeric skin.
Therefore, the well known fast reaction between an amine and an acid
chloride was attempted using silicone oil which is immiscible with
triethylene tetramine, but miscible with some acid chloride dissolving
organic solvents.

a.   Triethylene Tetramine Encapsulation

The wall forming reaction using triethylene
tetramine and sebacoyl chloride may be visualized ideally as follows:

$$4n \text{ Cl-}\overset{\overset{O}{\|}}{C}\text{-R-}\overset{\overset{O}{\|}}{C}\text{-Cl} + 2n \text{ H}_2\text{N-R-NH-R-NH-R-NH}_2 \longrightarrow$$

$$\left[\begin{array}{l} \text{-HN-R-N-R-N-R-NH-}\overset{\overset{O}{\|}}{C}\text{-R-}\overset{\overset{O}{\|}}{C} \\ \quad\quad\quad | \quad\quad | \\ \quad\quad\quad C=O \quad C=O \\ \quad\quad\quad | \quad\quad\;\; | \\ \quad\quad\quad R' \quad\quad R' \\ \quad\quad\quad | \quad\quad\;\; | \\ \quad\quad\quad C=O \quad C=O \quad\quad \overset{O}{\|}\quad\;\overset{O}{\|} \\ \text{- HN - R- N-R-N-R-NH C-R-C-} \end{array}\right]_n + 8n \text{ H Cl}$$

Where:

R is $(\text{CH}_2)_2$ and R' is $(\text{CH}_2)_8$

Quantities used:

25g triethylene tetramine (3. 6 g of which reacts with
the acid chloride).)3.27g of acid chloride reacts per
g. of amine based on above stoichiometry). 11.7 g
sebacoyl chloride in 50% n-hexane solution.

To silicone oil No. 200 was added with stirring a 50%
n-hexane solution containing 11.7g of sebacoyl chloride. Additional

n-hexane was added until a clear solution was obtained. To this was added 25g. of triethylene tetramine from a buret with the tip placed just below the liquid level and as close to the stirrer as possible. Stirring was continued at a moderate rate until a wall was formed around the amine droplets. The supernatant liquid was decanted and the capsules washed with n-hexane.

One batch of capsules was washed with water (Batch A). The second batch (Batch B) was dispersed in 3:1 (by volume) n-hexane-chloroform solution and 5g of triethylene tetramine in a 3:1 (by volume) n-hexane solution was then added to the dispersion in order to insure amine termination of the polyamide wall. Since the amine is already in excess this step may not be necessary. The supernatant liquid was decanted and the resulting capsules washed with a 3:1 (by volume) n-hexane-chloroform solution. The capsules were then dispersed in n-hexane and 5 ml. of toluene diisocyanate (TDI) was added for the purpose of obtaining an isocyanate extended polyamide wall. The supernatant liquid was then decanted and the resulting capsules washed in n-hexane then in water. The two batches of capsules were dried in a desiccator overnight and subsequent weighings taken in order to obtain a rough estimation of the weight percent internal phase lost with time.

Batch A		Batch B	
		TDI Treated	
Wt. % Loss	Time/hr.	Wt. % Loss	Time/hr.
6.8	8	9.3	8
20	73	27	73
21	96	27	96

From the above data, the TDI treatment makes little difference compared with the untreated capsules in the permeation of amine through the wall. Amine anaylsis of several batches of capsules prepared in a similar manner as above, indicated an average of 75-80% amine internal phase.

From these results it appears that wall strength and amine retention is adequate to render some type of post treatment of the wall very promising.

b. Attempted Hydrazine Encapsulation

Because of the fair degree of success obtained in encapsulating triethylene tetramine in the system described above, an attempt was made to encapsulate hydrazine with a small amount of triethylene tetramine added to induce some crosslinking.

To n-hexane was added 5.9g of sebacoyl chloride and while this solution was stirring silicone oil No. 200 was added in just enough quantity to keep the solution clear. An excess of hydrazine (10g. immiscible in both silicone oil and n-hexane) and 2.5g of triethylene tetramine were then added through a dropping funnel to

the stirring and chloride solution. The tip of the dropping funnel was placed as described above. Capsules and finely divided particles were formed. The supernatant liquid and finely divided particles were decanted and the heavier capsules remaining at the bottom were washed with n-hexane and then water filtered and dried. Microscopic examination revealed some liquid release when the capsules were crushed. A small amount of an oil layer (organic solvent residue) formed when the capsules were crushed in water and the resulting solution was basic to pH paper. An attempt was made to ignite the capsules over a direct flame and some slight sputtering was observed, but no direct ignition occurred. An unsuccessful attempt was made to ignite some crushed capsules spontaneously with nitrocellulose as reported in ONR Report No. 4. The capsules had no detectable irritating odor. After standing for a few days in a covered cardboard cylinder, the capsules were submitted for amine analysis and no free amine could be detected. The capsules, after standing, had the appearance of spherical empty shells.

4. Miscellaneous Encapsulation Studies

a. Phase Separation Study With Polyvinyl Cinnamate-Butarez System

An early attempt was made to phase separate a soluble polymer containing residual unsaturation around an internal phase (a solid in this case) followed by subsequent crosslinking.

Magnesium hydride (calculated for 80% internal phase) was dispersed in a 1% solution of polyvinyl cinnamate dissolved in 1-1 benzene-toluene and butarez was slowly added to phase out the polymer. When the concentration of butarez reached about 30% (based on total

-43-

liquid phases) microscopic examination revealed the formation of a thin tacky wall around the magnesium hydride particle in both single and aggregated states. When the butarez concentration reached 50% examination indicated the deposition of more wall material. The resulting dispersion was exposed to an ultra. violet source from a Gates lamp for one hour and examination indicated little or no change in the wall. The particles were in single and aggregated states and could not be isolated as non tacky entities.

b. Phase Separation Study Using Partially Miscible Liquid

It was felt that perhaps phase separation around an internal phase might occur, if a solvent which is immiscible with the internal phase, but partially miscible with the polymer solvent were slowly added in place of a phasing out polymer. In this case the internal phase would initially be in solution with the wall material and would have to phase out before the wall material upon addition of the phasing out component. It was hoped that the phasing out solvent would function at some critical point in the addition as a dispersing medium for the internal phase and then upon continued addition phase out the dissolved wall material around the resulting dispersed phase. The purpose for using a partially miscible solvent as opposed to a good solvent was to draw out the solvent for polymer wall gradually in order to avoid floculation of the polymer. An attempt was made to phase separate polyvinyl cinnamate dissolved in methyl ethyl ketone around n-hexane (internal phase) using water to slowly draw out methyl ethyl ketone. The solubility of water in methyl ethyl ketone at 25°C is about 10% and the solubility of methyl

-44-

ethyl ketone in water is about 22%.

To a solution of 5g. of polyvinyl cinnamate and 0.1g azobisisobutyronitrile in methyl ethyl ketone was added 25g n-hexane. The polymer precipitated out therefore a total of 100g of methyl ethyl ketone was used to redissolve most of the polymer. Water (500g) was slowly added to the stirring solution in order to disperse the n-hexane and slowly draw out the methyl ethyl ketone (final composition 20% methyl ethyl ketone in water) (solubility limit 22%) and deposit the polymer around the n-hexane droplets. During the water addition the mixture was simultaneously exposed to a Gates lamp ultra violet source placed beneath the reaction vessel. A swollen crosslinked polymer (no longer soluble in methyl ethyl ketone) phased out, but not around the n-hexane droplets. It is possible that the polymer phases out before the n-hexane droplets appear.

c.   Dispersion of a Latex-Encapsulation Attempt

When the methacrylation product of the 10-1 styrene-2-hydroxyethyl methacrylate copolymer (VIII-14) in organic solution was poured into water in an attempt to precipitate the copolymer a milky latex was formed, which had to be coagulated with a electrolyte in order to isolate the copolymer. At this time the thought came to mind that it might be possible to disperse this latex (as a finely divided colloidal suspension in water) in some dispersing medium to form latex droplets. Furthermore the residual methacrylic double bonds of the copolymer could be crosslinked thereby greatly decreasing the solubility of the copolymer and in the manner trap water inside the latex.

-45-

A concentrated acetone solution containing 1g. of the above copolymer (VIII-14) and a free radical initiator (azobisisobutyronitrile) was poured in 50 ml. of water while stirring and a milky latex was formed. This milky latex was dispersed in 100 ml. of silicone oil No. 200 and heated to 80^0C in a water bath for 4 hr. microscopic revealed a thim wrinkled wall around the dispersed droplets. An attempt to isolate the droplets from the continuous phase resulted in causing coalescence.

d. <u>Study of Post Treatment of a Capsular Wall-Graft Polymerization</u>

Gelatin capsules were used as a model in an attempt to post treat a formed capsule wall. Since gelatin contains some functional groups which are reducing agents, a free radical redox initiator was used in an attempt to graft polymerize a monomer on the gelatin wall. It was hoped that the redox initiating reaction would produce a free radical site at the gelatin wall followed by monomer addition at the wall site as shown by the following scheme.

$$\text{Gelatin} - RH + SO_{2 8}^{=} \longrightarrow \text{Gelatin} - R \cdot + \overset{-}{SO}_4 + HSO_4^-$$

$$\text{Gelatin} - R\cdot + n\ CH_2 = \underset{R'}{CH} \longrightarrow \text{Gelatin} - R - (CH_2 - \underset{R'}{CH-})_n$$
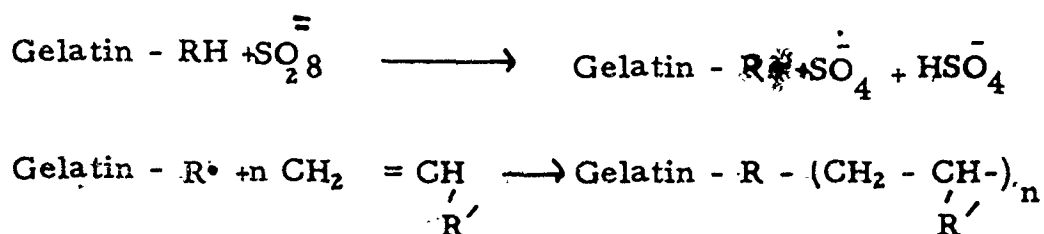
Where R H is a reducing Agent.

A batch of gelatin-2 way myvacet capsules suspend in the original water equilibrium medium was treated with a water solution of methacrylamide, potassium and ammonium persulfate and allowed to stir overnight. Upon examination it appeared that the gelatin wall

was stripped. A second batch of capsules was treated similarly using methylene bis acrylamide as the water soluble monomer is an attempt to form a crosslinked graft polymer. In this case the wall appeared to be swelled. When the supernatant liquid was decanted and the capsules washed with water, a solid gelled mass resulted on standing overnight.
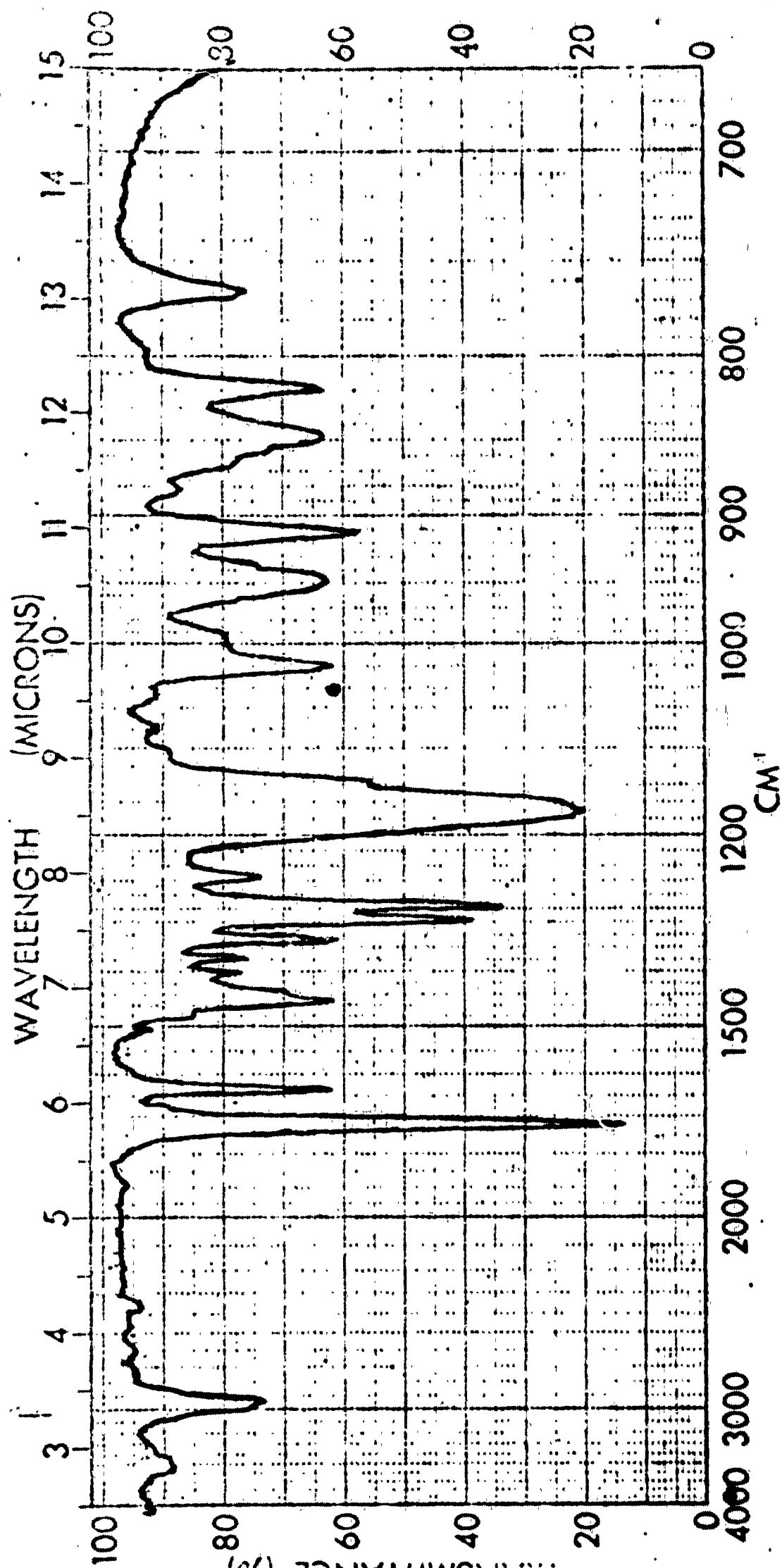
APPENDIX

INFRARED   SPECTRA
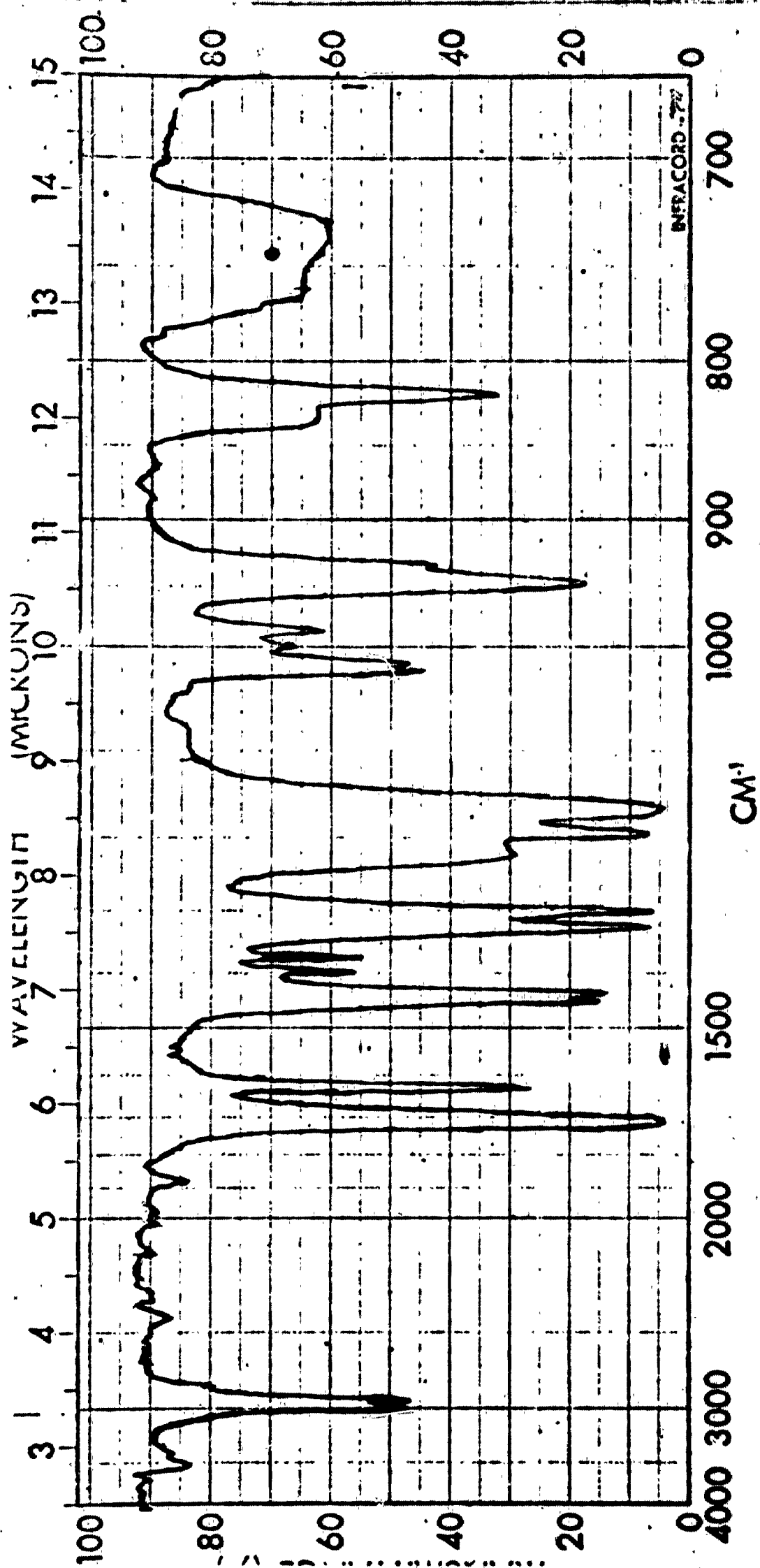
SPECTRUM NO. 1

SAMPLE _METHYL METHACRYLATE_

SPECTRUM NO.		ORIGIN		LEGEND		REMARKS
SAMPLE		PURITY		1.		
		PHASE		2.		
		THICKNESS		DATE		
				OPERATOR		

THE PERKIN-ELMER CORPORATION. NORWALK. CONN.

SPECTRUM NO.

SAMPLE

SPECTRUM NO. 2	ORIGIN	LEGEND	REMARKS
SAMPLE	PURITY	1.	
	PHASE SOLID SPREAD HSO2 DISK	2.	
GLYCOL MERCAPTALS	THICKNESS	DATE	
		OPERATOR	

SPECTRUM NO. 3

SAMPLE (II – 3)
FROM RADIAL HOMOGENATE
OF GLYCERIN ANHYDRATED

ORIGIN		LEGEND
		1.
PURITY		2.
PHASE		DATE
THICKNESS		OPERATOR

SPECTRUM NO.
SAMPLE

REMARKS
INFRARED SPECTRA
ON A HYDROCARBON
GREASE AND EPOXY CHIPS
PRESENT

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

INFRACORD 137-1281

SPECTRUM NO._____
SAMPLE_____

SPECTRUM NO. 4	ORIGIN	REMARKS
SAMPLE (X-4)		I. R. SAME AS
RESIDUE FROM RATIONS		METHALLY METHACRYLATE
POLYMERIZATION ATTEMPT		
OF METHALLYL METHACRYLATE		

	LEGEND
PURITY	1.
PHASE _____	2.
THICKNESS	DATE
	OPERATOR

CM⁻¹

PART NO 137-1754

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

WAVELENGTH (MICRONS)

CM⁻¹

100 80 60 40 20 0

3 4 5 6 7 8 9 10 11 12 13 14 15

3000 2000 1500 CM⁻¹ 1200 1000 900 800 700

SPECTRUM NO. _____
SAMPLE _____

SPECTRUM NO. 5	ORIGIN _____	LEGEND _____	REMARKS
SAMPLE		1. _____	
METHALLYL METHACRYLATE	PURITY _____	2. _____	
	PHASE LIQUID SPREAD ON SALT DISK	DATE _____	
	THICKNESS _____	OPERATOR _____	

THE PERKIN-ELMER CORPORATION NORWALK CONN.

WAVELENGTH (MICRONS)

3 4 5 6 7 8 9 10 11 12 13 14 15

4000 3000   2000   1500   1200   1000 900 800 700 CM⁻¹

100 80 60 40 20 0

SPECTRUM NO. 6	ORIGIN
SAMPLE (I-5)	
ACETONE SOLUBLE RESIDUE	PURITY
FROM CATIONIC POLYMERIZATION	
OF GLYCIDYL METHACRYLATE	
PHASE ON SALT DISK	DATE
THICKNESS	OPERATOR

SPECTRUM NO.
SAMPLE

LEGEND	REMARKS
1.	VERY LITTLE METHACRYLIC
	DOUBLE BOND PRESENT
2.	EPOXY GROUP PRESENT
	CARBONYL PRESENT
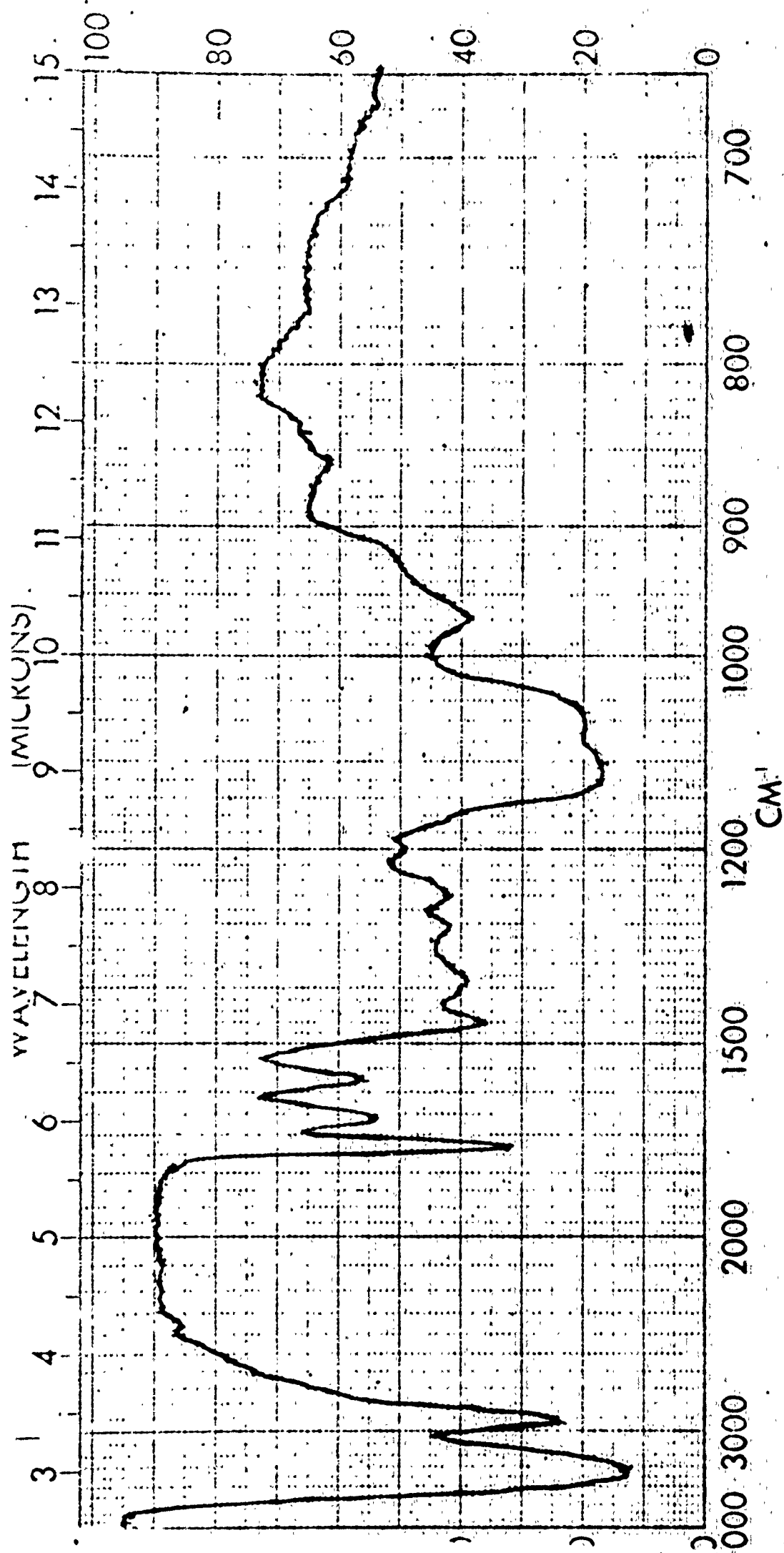
SPECTRUM NO.

SAMPLE

SPECTRUM NO. 7	ORIGIN	LEGEND	REMARKS
SAMPLE (I-7)		1.	METHACRYLIC DOUBLE BONDS
ACETONE INSOLUBLE RESIDUE	PURITY		PRESENT-NO EPOXY GROUPS
FROM CATIONIC POLYMERIZATION		2.	PRESENT-CARBONYL PRESENT
OF GLYCIDYL METHACRYLATE	VISCOUS RESIN SPREAD		
	PHASE ON SALT DISK	DATE	
	THICKNESS	OPERATOR	

THE PERKIN ELMER CORPORATION NEW YORK

WAVELENGTH (MICRONS)

3 4 5 6 7 8 9 10 11 12 13 14 15

100 80 60 40 20 0

4000 3000 2000 1500 CM⁻¹ 1200 1000 900 800 700

SPECTRUM NO. 8

SAMPLE
VINYL-2-CHLOROETHYL ETHER

ORIGIN

PURITY

PHASE   LIQUID SPREAD
        ON SALT DISK

THICKNESS

LEGEND
1.
2.
DATE
OPERATOR

REMARKS

SAMPLE

WAVELENGTH (MICRONS)

CM⁻¹

SPECTRUM NO. 9	ORIGIN	LEGEND
SAMPLE (II-9)		1.
2-VINYLOXYETHYL METHACRYLATE	PURITY b₂₀. 82-85°C./15mm n_D²⁵ = 1.4509	2.
	PHASE LIQUID SPREAD ON SALT DISK	DATE
THICKNESS		OPERATOR

SPECTRUM NO.
SAMPLE

REMARKS
VINYLOXY DOUBLE BOND PRESENT
METHACRYLIC DOUBLE BOND
PRESENT-CARBONYL PRESENT

WAVELENGTH (MICRONS)

CM⁻¹

SPECTRUM NO. 10	ORIGIN	LEGEND
SAMPLE (IV-10)		1.
CATIONIC POLYMERIZATION	PURITY	2.
PRODUCT OF 2-ETHOXY-		
ETHYL ALPHA MELATE	PHASE ON SALT DISK	DATE
THICKNESS		OPERATOR

SPECTRUM NO.
SAMPLE

REMARKS

VINYLOXY DOUBLE BOND
DISAPPEARED-METHACRYLIC DOUBLE
BOND PRESENT
CARBONYL PRESENT

SPECTRUM NO.
SAMPLE.

SPECTRUM NO. *11*	ORIGIN	LEGEND	REMARKS

SAMPLE ___(V-11)___

PRODUCT OF 10:1 STYRENE

2-VINYLOXYETHYL METHACRYLATE

PURITY ___

PHASE ___ CAST AS POLYMER FILM

THICKNESS ___

ORIGIN ___

DATE ___

OPERATOR ___

SPECTRUM NO.____
SAMPLE____

REMARKS	

LEGEND	
1.	
2.	

SPECTRUM NO. _12_	ORIGIN	PURITY

SAMPLE

2-HYDROXYETHY METHACRYLATE

PHASE LIQUID SPREAD
ON SALT DISK

THICKNESS____   DATE____

OPERATOR____

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WAVELENGTH (MICRONS)

INFRACORD — 137-1281

SPECTRUM NO.
SAMPLE

SPECTRUM NO. 13	ORIGIN
SAMPLE (JL.13)	
FREE RADICAL POLYMERIZATION	PURITY
PRODUCT OF 10:1 STYRENE-	
2-HYDROXYETHYL METHACRYLATE	PHASE CAST AS POLYMER FILM
	ON SALT DISK FROM
	METHYLENE CHLORIDE SOLUTION
THICKNESS	

REMARKS
HYDROXYL GROUP PRESENT
CARBONYL PRESENT
POLYSTYRENE PRESENT

LEGEND
1.
2.

DATE
OPERATOR

SPECTRUM NO.
SAMPLE _____

SPECTRUM NO. _14_	ORIGIN _____	LEGEND _____	REMARKS _____
SAMPLE __(VIII-14)__			SMALL AMOUNT OF BONDED
METHACRYLATION PRODUCT OF		1. _____	HYDROXY GROUP (WATER).
10:1 STYRENE—2—HYDROXY—	PURITY _____		INTRODUCED METHACRYLIC
ETHYL METHACRYLATE		2. _____	DOUBLE BOND — CARBONYL
	PHASE _CAST AS POLYMER FILM_	DATE _____	PRESENT — POLYSTYRENE PRESENT
	ON SALT DISK FROM		
	METHYLENE CHLORIDE SOLUTION		
THICKNESS _____		OPERATOR _____	

TRANSMITTANCE (%)

CM⁻¹

SPECTRUM NO. _15_

SAMPLE _(VII-15)_

FREE RADICAL POLYMERIZATION

PRODUCT OF 5:1 STYRENE-

2-HYDROXYETHYL METHACRYLATE

ORIGIN

PURITY

PHASE CAST AS POLYMER FILM
ON SALT DISK FROM
METHYLENE CHLORIDE SOLUTION

THICKNESS

LEGEND

1.

2.

DATE

OPERATOR

REMARKS

HYDROXY GROUP PRESENT

CARBONYL PRESENT

POLYSTYRENE PRESENT

SAMPLE

WAVELENGTH (MICRONS)

SPECTRUM NO._____
SAMPLE _____

SPECTRUM NO. 16 | ORIGIN _____

SAMPLE (TK-16)
METHACRYLATION PRODUCT OF

5:1 STYRENE-2-HYDROXY-
ETHYL METHACRYLATE

PURITY _____

CAST AS POLYMER FILM
PHASE ON SALT DISK FROM
METHYLENE CHLORIDE SOLUTION

THICKNESS _____

LEGEND _____

1. _____

2. _____

DATE _____

OPERATOR _____

REMARKS
TRACE OF WATER INTRODUCED
METHACRYLIC DOUBLE BOND
CARBONYL PRESENT
POLYSTYRENE PRESENT

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